Thirty-Ninth

symposium on

MOLECULAR
SPECTROSCOPY

THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO

June 11 - 15, 1984

DAAG29-83-C-0002

Under the Sponsorship of

the Department of Physics

the Department of Chemistry

the Graduate School

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and

the U.S. Army Research Office

SOME NOTES & NEWS

A SPECIAL NOTE OF THANKS:

It is a pleasure to acknowledge the time and enthusiastic help rendered by Professors Russell Pitzer and C. Weldon Mathews of the Department of Chemistry at the Ohio State University in taking care of the numerous details connected with the preparation of this year's program. It took a considerable amount of time and effort for Russ to organize the special seminars on Electronic Theory and Theoretical Chemistry. We are gratified that so many speakers arranged their itineraries so as to be able to participate in this symposium as well as in the Theoretical Chemistry Conference in Wyoming.

We take this opportunity to express our pleasure that, beginning this year, the Coblentz Society has decided to award their "Young Scientist Prize" at this symposium. We congratulate Steve Leone, the recipient of the 1984 Prize, and we hope that you will be able to attend the Award Lecture on the morning of Thursday, June 14.

1985 SYMPOSIUM ON MOLECULAR SPECTROSCOPY:

Next year's Molecular Spectroscopy Symposium will be the 40th of these annual events and as such it represents an important milestone in this series of meetings. We, hereby, urge all of you to come back and contribute to its success. We will do our best to make it a special event, but more than anything else it is your participation that will give it special significance.

So far, N. Bloembergen (Harvard), D. A. Ramsay (Ottawa, Canada), and E. Hirota (Japan) have accepted our invitations. A special seminar on "Time Resolved Raman Spectroscopy" is being organized with the help of Dr. G.N.R. Tripathi of Notre Dame University, and the interested speakers thus far are: R. Wilbrandt (Denmark), Shiro Maeda (Japan), G.N.R. Tripathi (USA), A. Laubereau and S. Schneider (West Germany).

START HERE **THIS DIMENSION MUST BE PRESERVED FOR EVERY ABSTRACT**

← 8 in. (=20 cm) →

THIS DIMENSION SHOULD BE 6 in. (= 15 cm) or less

HIGH RESOLUTION FOURIER SPECTROSCOPY OF THE Ar^+ LASER 5145 Å EXCITED I_2 FLUORESCENCE SPECTRUM

R. BACIS, S. CHURASSY, R. W. FIELD, J. B. KOFFEND, AND J. VERGES

This preliminary work demonstrates the feasibility of obtaining a high resolution spectrum of cw laser excited fluorescence using a Fourier spectrometer.

Using 1.3W of 5145 Å multimode power from an Ar^+ laser, fluorescence is excited mainly via the P(13) and R(15) (43,0) lines. Nearly all of the ~·' fluorescence lines [P(13), P(17), R(11), R(15)] originating from v' = 43 are observed   85. Their recorded full width at half maximum in the 7000-8000 cm⁻¹ regi~~

Rotational relaxation (ΔJ' -   rous odd-J" satellite lines.
The usual parameters are obtain.   rotation-vibration levels of
I_2 $X^1\Sigma^+$ through v" = 85.

This sample abstract gives the required format

Will be copied photographically

The vibrational line intens¹   ~ the alternation pattern predicted by the Franck-Condon factors of Tellingh·   ·ne agreement between measured and calculated intensities is only qualitative for ...gn v" values. This has important implications with respect to the I_2 laser gain measurements discussed in the following talk.

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[1] J. Tellinghuisen, J. Quant. Spect. Rad. Transf. 19, 149 (1978).

Address of Bacis and Churassy: Laboratoire de Spectrométrie Ionique et Moléculaire 43, bd du 11 Novembre 1918, 69621 - Villeurbanne, France.
Address of Field and Koffend: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.
Address of Verges: Laboratoire Aimé Cotton - C.N.R.S. II, Bâtiment 505, 91405 - Orsay, France.

Time required: 15, 10 or 5 min.

✱ Session in which paper is recommended for presentation:_____

Chemical formulas & sketches of molecular structures for larger molecules:

PLEASE NOTE:
1. Use good quality bond paper and an electric typewriter when preparing your Abstract. In the space for title and abstract you may include tables, equations and line drawings.

2. Send an original and one copy.

3. Please use a larger envelope for mailing. Do not fold.

4. Underline the name of the person who will be presenting the paper.

5. Include only the TITLE, AUTHORS' NAMES, and TEXT in the abstract. The author's affiliation should be given separately, as shown in the example.

6. Supply chemical formulas and rough sketches of structures of the larger molecules. This information is useful in arranging sessions.

General categories of sessions:

(1) Electronic (large molecules)   (6) Laser spectra   (11) Raman spectra
(2) Electronic (small molecules)   (7) Liquid state   (12) Solid state (electronic)
(3) Electronic (theory)   (8) Matrix spectra   (13) Solid state (infrared)
(4) Energy transfer   (9) Microwave   (14) Techniques
(5) High resolution IR & THEORY   (10) Molecular beam   (15) Vibrational analysis

PLEASE CHOOSE ONE OF THESE FIFTEEN CATEGORIES FOR YOUR PAPER AND GIVE THAT INFORMATION IN THE PLACE WHERE THE ✱ APPEARS ABOVE. THANK YOU.

MONDAY, JUNE 11, 1984 -- 9:30 A.M.

Auditorium, Independence Hall

Chairman: S. LESLIE BLATT, Department of Physics,
The Ohio State University, Columbus, Ohio.

Plenary Session

MA1.   LASER EXCITED FLUORESCENCE AND THE SPECTRA
OF SOME ALKALI METAL DIMERS.....................40 min.

R. F. BARROW, Physical Chemistry Laboratory,
Oxford University, South Parks Road, Oxford,
OX1 3QZ, England.

MA2.   HIGH INFORMATION INFRARED SPECTROSCOPY OF
SMALL MOLECULES................................40 min.

GUY GUELACHVILI, Laboratoire D'Infrarouge,
Universite de Paris-Sud, Batiment 350,
91405 Orsay Cedex, France.

PLEASE NOTE:

   ALL PAPERS IN THE Σ AND Π SESSIONS HAVE BEEN
SCHEDULED FOR PRESENTATION.   THE LISTS OF THESE
LATE PAPERS APPEAR ON PAGES 38-39 FOR Σ AND 40-41
FOR Π.   THE ABSTRACTS FOR THESE PAPERS HAVE BEEN
INCLUDED IN THE SESSIONS IN WHICH THE PAPERS ARE
ACTUALLY BEING PRESENTED.   THE LOGISTICS INVOLVED
IN THE PREPARATION OF THE PROGRAM AND ABSTRACTS
NECESSITATED THIS PROCEDURE.   IF THERE IS ANY CON-
FUSION, PLEASE SPEAK TO ME.

THANK YOU.

K. Narahari Rao

MONDAY, JUNE 11, 1984 -- 1:00 P.M.

Room 1153, Physics Laboratory

Chairman: DANIEL D. KONOWALOW, Department of Chemistry, State University
of New York at Binghamton, Binghamton, New York.

ME1. LARGE SCALE CI CALCULATIONS FOR DIATOMICS........INVITED PAPER............ 30 min.(1:00)

R. AHLRICHS, Institut fur Physikalische Chemie u. Elektrochemie
(Theoretische Chemie), D-7500 Karlsruhe, West Germany.

ME2. OPEN CORE DIATOMIC MOLECULES: LASER TECHNIQUES AND HERETICAL MODELS
....INVITED PAPER.........................30 min.(1:35)

ROBERT FIELD, Department of Chemistry, Massachusetts Institute of
Technology, Cambridge, Massachusetts, 02139.

ME3. DIFFUSE AND INTERFERENCE BANDS IN ALKALI METAL DIMERS....... ....20 min.(2:10)

J. T. BAHNS, W. T. LUH, A. M. LYYRA, P. D. KLEIBER, S. P. HENEGHAN,
W. C. STWALLEY, Iowa Laser Facility and Department of Chemistry,
University of Iowa, Iowa City, Iowa, 52242; G. PICHLER, Institute
of Physics, University of Zagreb, 41001 Zagreb, Yugoslavia; and
A. DECKERT, Bethel College, North Newton, Kansas, 67117.

ME4. NEW OPTICALLY-PUMPED LASERS IN THE $B^1\Pi_u$ - $X^1\Sigma_g^+$ AND $A^1\Sigma_u^+$ - $X^1\Sigma_g^+$ BANDS
OF Li_2..10 min.(2:32)

W. T. LUH, J. T. BAHNS, and W. C. STWALLEY, Iowa Laser Facility and
Department of Chemistry, University of Iowa, Iowa City, Iowa, 52242.

ME5. LASER SPECTROSCOPY OF THE DOUBLE MINIMUM POTENTIAL IN THE $E^1\Sigma_g^+$
STATE OF Li_2..15 min.(2:44)

R. A. BERNHEIM, L. P. GOLD, and C. A. TOMCZYK, Department of Chemistry,
Pennsylvania State University, University Park, Pennsylvania, 16802.

Intermission

ME6. ELECTRONIC TRANSITION DIPOLE MOMENT FUNCTIONS FOR NaK AND Li_2...............15 min.(3:15)

LYN B. RATCLIFF, DANIEL D. KONOWALOW, Department of Chemistry, State
University of New York at Binghamton, Binghamton, New York, 13901;
and WALTER J. STEVENS, Molecular Spectroscopy Division, National
Bureau of Standards, Washington, D.C., 20234.

ME7. HIGH RESOLUTION FOURIER SPECTROSCOPY OF THE LASER EXCITED Cs_2
FLUORESCENCE SPECTRUM: FIVE NEW ELECTRONIC STATES.........................10 min.(3:32)

C. CREPIN, J. VERGES, Laboratoire Aimé-Cotton - CNRS II, 91405 Orsay,
France; and C. AMIOT, Laboratoire de Physique Moléculaire et d'Optique
Atmosphérique, Campus d'Orsay, 91405 Orsay, France.

ME8. AN EXACT SOLUTION OF THE VIBRATIONAL MOTION OF A DISSOCIATIVE STATE.........15 min.(3:44)

E. E. LAFLEUR and L. Y. CHOW CHIU, Department of Chemistry, Howard
University, Washington, D.C., 20059.

ME9. CALCULATION OF POTENTIAL ENERGY CURVES & FRANCK CONDON FACTORS FOR
DIATOMIC MOLECULES BY USE OF THE INVERTED PERTURBATION TECHNIQUE............10 min.(4:01)

ERNEST A. DORKO, LYLE L. RUTGER, and JOSEPH J. POW, Department of
Engineering Physics, Air Force Institute of Technology, Wright-
Patterson Air Force Base, Ohio, 45433.

ME10. DIPOLE MOMENTS OF THE GROUND AND EXCITED VIBRATIONAL STATES OF OH AND OD....15 min.(4:13)

K. I. PETERSON, G. T. FRASER, and W. KLEMPERER, Department of
Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

ME11. ACCURATE MULTIREFERENCE-CI CALCULATIONS OF RADIATIVE TRANSITION
PROBABILITIES. I. VIBRATIONAL TRANSITIONS WITHIN THE ELECTRONIC GROUND
STATES OF OH, OH^-, OH^+, HF^+, AND HCl^+......... ....(4:30)-(5:00)

H.-J. WERNER, University Chemical Laboratory, Cambridge, CB2 1EW,
England; P. ROSMUS, and E.-A. REINSCH, Fachbereich Chemie der
Universitaet Frankfurt, D-6000 Frankfurt, West Germany.

ME12. ACCURATE MULTIREFERENCE-CI CALCULATIONS OF RADIATIVE TRANSITION
PROBABILITIES. II. ELECTRONIC TRANSITIONS BETWEEN THE A AND X STATES OF
CH, OH, HF^+, AND HCl^+.......... ....

H.-J. WERNER, University Chemical Laboratory, Cambridge, CB2 1EW,
England; P. ROSMUS, Fachbereich Chemie der Universitaet Frankfurt,
D-6000 Frankfurt, West Germany; W. SCHAETZL, and W. MEYER, Fachbereich
Chemie der Universitaet Kaiserslautern, D-6750 Kaiserslautern,
West Germany.

ME13. ACCURATE MULTIREFERENCE-CI CALCULATIONS OF RADIATIVE TRANSITION
PROBABILITIES. III. ELECTRONIC TRANSITIONS BETWEEN THE A AND X STATES OF
CN, THE X,A, AND B STATES OF C_2^-, AND THE LOWEST FIVE TRIPLET STATES OF N_2..

H.-J. WERNER, University Chemical Laboratory, Cambridge, CB2 1EW,
England; P. ROSMUS, J. KALCHER, E.-A. REINSCH, Fachbereich Chemie der
Universitaet Frankfurt, D-6000 Frankfurt, West Germany; P. J. HAY,
and D. C. CARTWRIGHT, Los Alamos National Laboratory, Los Alamos,
New Mexico, 87545.

ME14. Σ12 will be presented here (H. J. Vedder)................................15 min.(5:00)

MONDAY, JUNE 11, 1984 -- 1:00 P.M.

Room 1109, Physics Laboratory

Chairman Before Intermission: RUSSELL BARNES, Battelle Columbus Laboratories, Columbus, Ohio.

Chairman After Intermission: J. GELFAND, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey.

MF1. PRESSURE BROADENING AND INTENSITY MEASUREMENTS FOR THE 2-0 BAND OF NO.......15 min.(1:00)

A. G. MAKI and A. S. PINE, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C., 20234.

MF2. MEASUREMENTS OF PRESSURE BROADENING BY POLAR GASES.........................10 min.(1:17)

M.A.H. SMITH, G. A. HARVEY, NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665; D. J. RICHARDSON, R. E. THOMPSON, and C. H. SUTTON, Systems and Applied Sciences Corporation, Hampton, Virginia, 23666.

MF3. HCℓ FUNDAMENTAL ROVIBRATIONAL SELF-BROADENING COEFFICIENTS BETWEEN 200 K AND 300 K..10 min.(1:29)

C. CHACKERIAN, JR., D. GOORVITCH, and L. P. GIVER, Astrophysical Experiments Branch, NASA Ames Research Center, Moffett Field, California, 94035.

MF4. PRESSURE BROADENED LINEWIDTHS AND ABSORPTION INTENSITIES OF THE FUNDAMENTAL AND FIRST OVERTONE BAND OF DF...10 min.(1:41)

J. GELFAND, K. VERGES, and T. BEVILACQUA, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey, 08544.

MF5. NITROGEN-BROADENED LINES OF MONODEUTERATED METHANE IN THE 1.6 μm REGION..... 5 min.(1:53)

BARRY L. LUTZ, Lowell Observatory, Flagstaff, Arizona, 86002.

MF6. INTENSITY MEASUREMENTS IN THE 3 μm BANDS OF $^{12}CH_4$ AND $^{12}C_2H_2$ AT LOW TEMPERATURES..15 min.(2:00)

P. VARANASI, S. CHUDAMANI, Laboratory for Planetary Atmospheres Research, State University of New York, Stony Brook, New York, 11794; L. P. GIVER and F.P.J. VALERO, Astrophysical Experiments Branch, NASA Ames Research Center, Moffett Field, California, 92035.

MF7. ABSOLUTE LINE STRENGTHS OF PHOSPHINE GAS IN THE 5 MICRON REGION.............10 min.(2:17)

R. W. LOVEJOY, R. D. SCHAEFFER, Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania, 18015; and D. L. FRASCO, Department of Chemistry, Whitman College, Walla Walla, Washington, 99362.

MF8. THEORETICAL N_2-, O_2-, AND AIR-BROADENED HALFWIDTHS OF $^{16}O_3$ CALCULATED BY QUANTUM FOURIER TRANSFORM THEORY WITH REALISTIC COLLISION DYNAMICS..........10 min.(2:29)

R. R. GAMACHE, Center for Atmospheric Research, University of Lowell Research Foundation, Lowell, Massachusetts, 01854; R. W. DAVIES, GTE Sylvania, 40 Sylvan Road, Waltham, Massachusetts, 02154; and L. S. ROTHMAN, Optical Physics Division, Air Force Geophysics Laboratory, Hanscom AFB, Bedford, Massachusetts, 01731.

MF9. DIODE LASER STUDIES OF ISOTOPIC OZONE BANDS NEAR 10 μm......................10 min.(2:41)

V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; B. S. WILLIAMS, M.A.H. SMITH, C. P. RINSLAND, J. M. HOELL, and R. S. ROGOWSKI, NASA Langley Research Center, Hampton, Virginia, 23665.

Intermission

MF10. TUNABLE DIODE LASER MEASUREMENTS OF INTENSITIES AND AIR-BROADENED HALFWIDTHS OF THE ν_2 BAND OF HDO: RESULTS AND THEIR APPLICATION TO THE ANALYSIS OF STRATOSPHERIC SOLAR ABSORPTION SPECTRA.....................................10 min.(3:10)

C. P. RINSLAND, NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665; A. GOLDMAN, F. J. MURCRAY, D. G. MURCRAY, Department of Physics, University of Denver, Denver, Colorado, 80208; V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; B. FRIDOVICH, NOAA/NESDIS, FOB#4, E/RA21, Washington, D.C., 20233; M. T. COFFEY and W. G. MANKIN, National Center for Atmospheric Research, Code 1302, Boulder, Colorado, 80307.

MF11. THE PRECISION OF THE LINE PARAMETERS RETRIEVED FROM A LORENTZ
ABSORPTION LINE...15 min.(3:22)

> N. TU and J. H. SHAW, Department of Physics, The Ohio State University,
> Columbus, Ohio, 43210.

MF12. IDENTIFICATION AND INTENSITIES OF THE "FORBIDDEN" $03^30 \leftarrow 00^00$ BAND OF
$^{12}C^{16}O_2$..10 min.(3:39)

> D. CHRIS BENNER, Department of Physics, College of William and Mary,
> Williamsburg, Virginia, 23185; and C. P. RINSLAND, NASA Langley
> Research Center, Mail Stop 401A, Hampton, Virginia, 23665.

MF13. ANALYSIS OF CARBON DIOXIDE BANDS NEAR 2.2 μm...............................10 min.(3:51)

> M. ABUBAKAR, M. L. HOKE, R. L. HAWKINS, and J. H. SHAW, Department of
> Physics, The Ohio State University, Columbus, Ohio, 43210.

MF14. HIGH TEMPERATURE $^{12}C^{16}O^{18}O$ AND $^{12}C^{18}O_2$ SPECTRA IN THE 2.7 μm REGION.........10 min.(4:03)

> M. P. ESPLIN, Stewart Radiance Laboratory, Utah State University,
> Bedford, Massachusetts, 01730; and L. S. ROTHMAN, Optical Physics
> Division, U.S. Air Force Geophysics Laboratory, Hanscom Air Force
> Base, Massachusetts, 01731.

MF15. MOLECULAR PARAMETERS FOR CARBON DIOXIDE BANDS IN THE 3.73-4.17 μm
SPECTRAL REGION.. 5 min.(4:15)

> V. MALATHY DEVI, D. C. BENNER, Department of Physics, College of
> William and Mary, Williamsburg, Virginia, 23185; and C. P. RINSLAND,
> NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665.

MF16. A CONSISTENT GLOBAL SOLUTION OF $^{12}C^{16}O_2$ VIBRATIONAL ENERGY LEVELS AND
BAND STRENGTHS..15 min.(4:22)

> R. B. WATTSON, Visidyne, Incorporated, 5 Corporate Place, South Bedford
> Street, Burlington, Massachusetts, 01803; and L. S. ROTHMAN, Optics
> Division, Air Force Geophysics Laboratory, Hanscom Air Force Base,
> Massachusetts, 01731.

MF17. A STUDY OF THE STRENGTHS AND WIDTHS OF LINES IN THE $10_1 \mu$m N_2O BANDS........10 min.(4:39)

> SHANXIONG SHEN, ZENGXIN GUO, and I-SHAN CHENG, Department of Physics,
> East China Normal University, Shanghai 200062, People's Republic of
> China.

MF18. THE EFFECT OF TEMPERATURE ON THE HALF-WIDTH OF THE ETHYLENE ABSORPTION
AT 10 μ...10 min.(4:51)

> SHANXIONG SHEN, CAI PEIPEI, ZHANG HANSHENG, and I-SHAN CHENG, Department
> of Physics, East China Normal University, Shanghai 200062, People's
> Republic of China.

MF19. T2 will be presented here (R. W. Davies)....................................   (5:02)

MF20. T2a will be presented here (S. A. Clough)...................................

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Room 1005, Physics Laboratory

Chairman Before Intermission: FRANK C. DeLUCIA, Department of Physics,
Duke University, Durham, North Carolina.

Chairman After Intermission: MANFRED WINNEWISSER, Physikalisch-Chemisches
Institut, Justus-Liebig-Universität, D-6300
Giessen, West Germany.

MG1. PULSED FOURIER TRANSFORM MICROWAVE SPECTROSCOPY AT 140 GHz...................15 min.(1:00)

W. F. KOLBE and B. LESKOVAR, Lawrence Berkeley Laboratory, University
of California, Berkeley, California, 94720.

MG2. THE MICROWAVE SPECTRUM OF THE MONO-CHLOROMETHYL RADICAL, CH_2Cl...............10 min.(1:17)

Y. ENDO, S. SAITO, and E. HIROTA, Institute for Molecular Science,
Okazaki 444, Japan.

MG3. THE MICROWAVE SPECTRUM OF THE VINOXY RADICAL, CH_2CHO.......................10 min.(1:29)

Y. ENDO, S. SAITO, and E. HIROTA, Institute for Molecular Science,
Okazaki 444, Japan.

MG4. THE MICROWAVE SPECTRUM OF THE METHOXY RADICAL, CH_3O: HYPERFINE STRUCTURE
AND JAHN-TELLER INTERACTION...15 min.(1:41)

Y. ENDO, S. SAITO, and E. HIROTA, Institute for Molecular Science,
Okazaki 444, Japan.

MG5. THE MILLIMETER- AND SUBMILLIMETERWAVE SPECTRUM OF METHYL HYDROPEROXIDE......15 min.(1:58)

C. E. BLOM, Physikalisch-Chemisches Institut, Justus Liebig
Universität Giessen, D-6300 Giessen, West Germany.

MG6. MICROWAVE AND MILLIMETER WAVE SPECTRA OF ISOTOPICALLY SUBSTITUTED
DIAZIRINE SPECIES: ROTATIONAL AND HYPERFINE STRUCTURE ANALYSIS AND
MOLECULAR STRUCTURE...15 min.(2:15)

K. MÖLLER, U. P. VERMA, J. VOGT, M. WINNEWISSER, Physikalisch-
Chemisches Institut, Justus-Liebig-Universität, D-6300 Giessen,
West Germany; and J. J. CHRISTIANSEN, Department of Chemistry,
The Royal Danish School of Educational Studies, DK-2400
Copenhagen NV, Denmark.

MG7. MICROWAVE SPECTRUM OF METHOXYBORANE, CH_3OBH_2..............................10 min.(2:32)

Y. KAWASHIMA, Ikutoku Technical University, 1030 Shimo-Ogino,
Atsugi, Kanagawa, 243-02, Japan; H. TAKEO, and C. MATSUMURA,
National Chemical Laboratory for Industry, Tsukuba, Ibaraki,
305, Japan.

Intermission

MG8. SPECTROSCOPY OF SMALL, FUNDAMENTAL SPECIES IN THE MILLIMETER AND
SUBMILLIMETER SPECTRAL REGION...15 min.(3:00)

GRANT M. PLUMMER, J. K. MESSER, ERIC HERBST, FRANK C. DE LUCIA,
Department of Physics, Duke University, Durham, North Carolina, 27706;
PAUL HELMINGER, Department of Physics, University of South Alabama,
Mobile, Alabama, 36688; GEOFFREY A. BLAKE, Department of Chemistry,
California Institute of Technology, Pasadena, California, 91125;
and K.V.L.N. SASTRY, Department of Physics, University of Brunswick,
Fredericton, New Brunswick, Canada, E3B 5A3.

MG9. STUDIES OF CO NEAR 4 K...15 min.(3:17)

J. K. MESSER and FRANK C. DE LUCIA, Department of Physics, Duke
University, Durham, North Carolina, 27706.

MG10. APPLICATIONS OF THE AC STARK EFFECT IN THE MILLIMETER AND SUBMILLIMETER
REGION..15 min.(3:34)

DAVID D. SKATRUD and FRANK C. DE LUCIA, Department of Physics, Duke
University, Durham, North Carolina, 27706.

J. M. WARE and J. A. ROBERTS, Department of Physics, North Texas
State University, Denton, Texas, 76203.

E. A. COHEN, H. M. PICKETT, J. S. MARGOLIS, and C. CHIU, Jet Propulsion
Laboratory, 4800 Oak Grove Drive, Pasadena, California, 91109.

W. G. READ, E. A. COHEN, and H. M. PICKETT, Jet Propulsion Laboratory,
4800 Oak Grove Drive, Pasadena, California, 91109.

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MONDAY, JUNE 11, 1984 -- 1:00 P.M.

Room 1008, Evans Chemical Laboratory

Chairman Before Intermission: JOSEPH K. McDONALD, Research Directorate, U.S. Missile Laboratory, U.S. Army Missile Command, Redstone Arsenal, Alabama.

Chairman After Intermission: P. D. MAKER, Ford Motor Company, Dearborn, Michigan.

MH1. EXCITED VIBRATIONAL STATES NEAR DISSOCIATION IN WEAKLY BOUND TRIATOMIC SYSTEMS..10 min.(1:00)

> J. G. FREY, MMRD 70A-4418, Lawrence Berkeley Laboratory, University of California, Berkeley, California, 94709.

MH2. AN AB INITIO STUDY OF THE HARMONIC FORCE FIELDS AND VIBRATIONAL FREQUENCIES OF CF_4 AND SiF_4...15 min.(1:12)

> L. A. CURTISS, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois, 60439.

MH3. AN ADJUSTED VALENCE FORCE FIELD(AVFF)FOR POLYATOMIC MOLECULES...............15 min.(1:29)

> V. A. MARONI, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois, 60439.

MH4. THE VIBRATIONAL SPECTRUM OF FORMYL BROMIDE, HBrCO..........................15 min.(1:46)

> P. D. MAKER, H. NIKI, L. P. BREITENBACH, and C. M. SAVAGE, S3078 Scientific Research Laboratory, Ford Motor Company, Box 2053, Dearborn, Michigan, 48121.

MH5. VIBRATIONAL SPECTRA OF CYCLOPROPYL CHLORIDE.................................10 min.(2:03)

> C. J. WURREY, P. M. GREEN, Department of Chemistry, University of Missouri, Kansas City, Missouri, 64110; and V. F. KALASINSKY, Department of Chemistry, Mississippi State University, Mississippi State, Mississippi, 39762.

MH6. VIBRATIONAL SPECTRA AND BARRIER TO INTERNAL ROTATION OF VINYLSILANE.........15 min.(2:15)

> J. A. SMITH, S. E. RODGERS, and V. F. KALASINSKY, Department of Chemistry, Mississippi State University, Mississippi State, Mississippi, 39762.

Intermission

MH7. VIBRATIONAL SPECTRA OF PERFLUOROCYCLOPROPENE: A POTENTIAL FUNCTION FOR THIS SUBSTANCE AND RELATED CYCLOPROPENES...............................10 min.(3:00)

> NORMAN C. CRAIG, GINI F. FLEMING, and JULIANTO PRANATA, Department of Chemistry, Oberlin College, Oberlin, Ohio, 44074.

MH8. VIBRATIONAL SPECTRA OF THE PERFLUOROCYCLOPROPENYL CATION: A POTENTIAL FUNCTION FOR THIS SUBSTANCE AND RELATED CATIONS...........................10 min.(3:12)

> NORMAN C. CRAIG, GINI F. FLEMING, and JULIANTO PRANATA, Department of Chemistry, Oberlin College, Oberlin, Ohio, 44074.

MH9. MEDIUM RESOLUTION FAR INFRARED SPECTROSCOPY OF GASEOUS CYCLOPROPYL-ISOTHIOCYANATE: ANALYSIS OF LARGE AMPLITUDE ANHARMONIC VIBRATIONS..........10 min.(3:24)

> D. J. GERSON, IBM Instruments Incorporated, P. O. Box 332, Danbury, Connecticut, 06810.

MH10. CONFORMATIONAL STABILITY AND BARRIERS TO INTERNAL ROTATION OF ISOPROPYL CARBOXALDEHYDE..15 min.(3:36)

> J. R. DURIG, G. A. GUIRGIS, T. S. LITTLE, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208; and O. L. STIEFVATER, School of Physical and Molecular Science, University College of North Wales, Bangor, Gurynodd, Wales, United Kingdom.

MH11. INFRARED AND RAMAN SPECTRA OF GASEOUS AND SOLID NITROSYL CHLORIDE...........15 min.(3:53)

> J. K. McDONALD, J. A. MERRITT, Commander, U. S. Army Missile Command, ATTN: DRSMI-RRD, Redstone Arsenal, Alabama, 35898; and J. R. DURIG, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

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TUESDAY, JUNE 12, 1984 -- 8:30 A.M.

Room 1153, Physics Laboratory

Chairman Before Intermission: T. K. BALASUBRAMANIAN, Bhabha Atomic Research Centre, Bombay, India.

Chairman After Intermission: JAMES R. GAINES, Department of Physics, The Ohio State University, Columbus, Ohio.

SEMINAR OF INVITED PAPERS ON HYDROGEN

TA1. ORIENTATIONAL PROPERTIES OF THE MOLECULES IN SOLID HYDROGEN.................40 min.(8:30)

J. VAN KRANENDONK, Department of Physics, University of Toronto, Toronto, Ontario, Canada, M5S 1A7.

TA2. ORIENTATIONAL ORDERING OF ORTHO-H_2 IN SOLID H_2.............................30 min.(9:15)

H. MEYER, Department of Physics, Duke University, Durham, North Carolina, 27706.

TA3. THE RELATIONSHIP BETWEEN THE CALCULATED ABSORPTION COEFFICIENT FOR PURE ROTATIONAL TRANSITIONS IN SOLID H_2 AND THE PHONON DENSITY OF STATES........20 min.(9:50)

JAMES R. GAINES, S. I. LEE, and K. NARAHARI RAO, Department of Physics, The Ohio State University, Columbus, Ohio, 43210.

Intermission

TA4. MULTIPOLE MOMENTS OF H_2 AND ITS ISOTOPES................................30 min.(10:30)

R. H. TIPPING, Department of Physics, University of Alabama, University, Alabama, 35486.

TA5. NEW OVERTONE SPECTRA OF SOLID HYDROGENS...................................30 min.(11:05)

C.K.N. PATEL, AT&T Bell Laboratories, Murray Hill, New Jersey, 07974.

TA6. THE INDUCED SPECTRUM OF HYDROGEN IN THE CONDENSED PHASE AND ITS IMPLICATIONS FOR THE STUDY OF THE SOLID STATE OF H_2........................15 min.(11:40)

T. K. BALASUBRAMANIAN, Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, Bombay-400 085, India.

TUESDAY, JUNE 12, 1984 -- 9:30 A.M.

Room 1009, Physics Laboratory

Chairman: LARY W. PINKLEY, Nichols Research Corporation, Huntsville, Alabama.

TB1. ABSORPTION SPECTRUM OF NITROUS OXIDE IN THE REGION OF ν_1 AND $2\nu_2$............10 min. (9:30)

> L. HENRY, J. L. TEFFO, A. VALENTIN, Laboratoire de Spectronomie
> Moléculaire, Université Pierre et Marie Curie, 75230 Paris, France;
> and T. K. McCUBBIN, Department of Physics, Pennsylvania State
> University, University Park, Pennsylvania, 16802.

TB2. HIGH RESOLUTION FOURIER TRANSFORM STUDY OF THE MID-INFRARED BANDS
OF CYCLOPROPANE..15 min. (9:42)

> J. PLÍVA, Department of Physics, Pennsylvania State University,
> University Park, Pennsylvania, 16802; and J.W.C. JOHNS, Herzberg
> Institute of Astrophysics, National Research Council of Canada,
> 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6.

TB3. ANALYSIS OF THE PERPENDICULAR BANDS OF CYCLOPROPANE IN THE 3.3 μm REGION....15 min. (9:59)

> D. W. MERDES, J. PLÍVA, Department of Physics, Pennsylvania State
> University, University Park, Pennsylvania, 16802; and A. S. PINE,
> Molecular Spectroscopy Division, National Bureau of Standards,
> Washington, D.C., 20234.

TB4. ANALYSIS OF THE ν_9 AND ν_{10} BANDS OF ALLENE................................15 min. (10:16)

> J. CHAZELAS, A. VALENTIN, L. HENRY, Laboratoire de Spectronomie
> Moléculaire CNRS 060136, Université Pierre et Marie Curie, 75230
> Paris, France; and J. PLÍVA, Department of Physics, Pennsylvania
> State University, University Park, Pennsylvania, 16802.

Intermission

TB5. THE HIGH RESOLUTION SPECTRUM OF THE 4^1_0 BAND OF THE UNSTABLE MOLECULE
HBF_2 NEAR 10.8 μm..15 min. (10:45)

> M.C.L. GERRY, W. LEWIS-BEVAN, A. J. MERER, and N.P.C. WESTWOOD,
> Department of Chemistry, University of British Columbia, Vancouver,
> British Columbia, Canada, V6T 1Y6.

TB6. THE HIGH RESOLUTION SPECTRUM OF THE 4^1_0 BAND OF THE UNSTABLE MOLECULE
H_2NBH_2 NEAR 7.5 μm..15 min. (11:02)

> M.C.L. GERRY, W. LEWIS-BEVAN, A. J. MERER, and N.P.C. WESTWOOD,
> Department of Chemistry, University of British Columbia, Vancouver,
> British Columbia, Canada, V6T 1Y6.

TB7. SIMULTANEOUS ANALYSIS OF THE ν_2, ν_3, ν_5 AND ν_6 BANDS OF CD_3F................15 min. (11:19)

> L. HALONEN, Department of Chemistry, Helsinki University of Technology,
> SF-02150 Espoo 15, Finland.

TB8. HIGH RESOLUTION INFRARED SPECTRUM OF DNO_2 BELOW 1200 CM^{-1}...................10 min. (11:36)

> L. HALONEN, Department of Chemistry, Helsinki University of Technology,
> SF-02150 Espoo 15, Finland.

TB9. DIODE LASER AND FT-IR SPECTRA OF THE ν_4, ν_6 AND ν_3 BANDS OF FORMALDEHYDE....10 min. (11:48)

> S. D. NADLER, S. J. DAUNT, Department of Chemistry, Concordia University,
> Montréal, Québec, Canada, H3G 1M8; D. C. REUTER, NASA Goddard Space Flight
> Center, Laboratory for Atmospheric Sciences, Code 911, Greenbelt, Maryland,
> 20771; and J.W.C. JOHNS, Herzberg Institute of Astrophysics, National
> Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada,
> K1A OR6.

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TUESDAY, JUNE 12, 1984 -- 9:30 A.M.

Room 1005, Physics Laboratory

Chairman: COLAN LINTON, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada.

TC1. THE $b^4\Sigma^- - a^4\pi_i$ TRANSITION OF THE NO MOLECULE...............................15 min. (9:30)

K. P. HUBER, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6.

TC2. HIGH RESOLUTION UV LASER SPECTROSCOPY ON THE NH FREE RADICAL................15 min. (9:47)

W. UBACHS, J. J. TER MEULEN, and A. DYMANUS, Fysisch Laboratorium, Katholieke Universiteit, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

TC3. THE LOCATION AND PARENTAGE OF ELECTRONIC TRANSITIONS OF HETERONUCLEAR DIATOMIC MOLECULES CONTAINING TRANSITION METALS, USING EMPIRICAL METHODS....10 min. (10:04)

RONALD C. CARLSON, Department of Chemistry, University of California, and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California, 94720; and THOMAS M. DUNN, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

TC4. LIFETIMES AND MAGNETIC MOMENTS OF PERTURBED ROTATIONAL LEVELS OF $A^1\Sigma^+$ BaO...15 min. (10:16)

S. D. DARRAH and S. J. SILVERS, Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia, 23284.

TC5. LIF STUDIES OF GROUP IIA DIMERS PRODUCED BY LASER VAPORIZATION OF THE METALS...15 min. (10:33)

V. E. BONDYBEY, AT&T Bell Laboratories, Murray Hill, New Jersey, 07974.

TC6. THE RED ABSORPTION SYSTEM OF THE Ca_2 MOLECULE...............................15 min. (10:50)

R. THOMAS HOFMANN and DAVID O. HARRIS, Quantum Institute and the Department of Chemistry, University of California, Santa Barbara, California, 93106.

TC7. LASER SPECTROSCOPY OF NiO: ROTATIONAL ANALYSIS OF THE SYSTEM IV IN THE 5170 - 5500 Å REGION...15 min. (11:07)

VOJISLAV I. SRDANOV and DAVID O. HARRIS, Quantum Institute and the Department of Chemistry, University of California, Santa Barbara, California, 93106.

TC8. POLARIZATION SPECTROSCOPY OF SrCl: THE $B^2\Sigma^+ - X^2\Sigma^+$ SYSTEM..................15 min. (11:24)

W. E. ERNST and J. O. SCHRÖDER, Institut für Molekülphysik, Freie Universität Berlin, D-1000 Berlin 33, Germany.

TC9. HIGH RESOLUTION LASER PHOTOACOUSTIC SPECTROSCOPY OF ICℓ.....................15 min. (11:41)

D. KUMAR, R. V. NAUMAN, S. P. McGLYNN, Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana, 70802; and P. VENKATESWARLU, Department of Physics, Alabama A & M University, Normal(Huntsville), Alabama, 35762.

TUESDAY, JUNE 12, 1984 -- 8:30 A.M.

Room 1008, Evans Chemical Laboratory

Chairman: I. SHAVITT, Department of Chemistry, The Ohio State University, Columbus, Ohio.

SEMINAR OF INVITED PAPERS ON THEORETICAL CHEMISTRY

TD1. VIBRATION-ROTATION HAMILTONIANS AND THE RENNER-TELLER EFFECT.................30 min.(8:30)

N. C. HANDY, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, United Kingdom.

TD2. CASSCF AND MULTI-REFERENCE CI CALCULATIONS OF INFRA-RED BANDSTRENGTHS FOR HCN...30 min.(9:05)

J. ALMLÖF, Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway; P. SIEGBAHN, Institute of Theoretical Physics, University of Stockholm, S-11346 Stockholm, Sweden; M. LARSSON, Research Institute of Physics, S-10405 Stockholm, Sweden; U. JØRGENSEN, and B. GUSTAFSSON, Department of Astronomy, University of Uppsala, S-75120 Uppsala, Sweden.

Intermission

TD3. THEORETICAL INVESTIGATION OF ALKALI DIMERS: POTENTIAL CURVES, TRANSITION MOMENTS, COUPLING ELEMENTS, LIFETIMES, AND PERTURBATIONS...30 min.(10:00)

WILFRIED MEYER, Fachbereich Chemie der Universitaet Kaiserslautern, D-6750 Kaiserslautern, West Germany.

TD4. EXCITED STATES IN SMALL ORGANIC MOLECULES STUDIED BY CASSCF- AND CI-TYPE WAVE FUNCTIONS...30 min.(10:35)

P.-Å. MALMQVIST and B. O. ROOS, Department of Theoretical Chemistry, Chemical Centre, S-220 07 Lund, Sweden.

TD5. EXCITED STATES AND PHOTOCHEMICAL REACTIONS OF ORGANOMETALLICS: THEORETICAL INVESTIGATIONS..30 min.(11:10)

A. VEILLARD, E.R. 139 du CNRS, Institut Le Bel, Université L. Pasteur, 67000 Strasbourg, France.

TD6. ΠI will be presented here (W. Meyer)..10 min.(11:45)

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Room 1153, Physics Laboratory

Chairman: RANDALL D. KNIGHT, Department of Physics, The Ohio State University, Columbus, Ohio.

TE1. FORBIDDEN ROTATIONAL TRANSITIONS OF H_3^+......................................10 min.(1:30)

F. S. PAN and T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637.

TE2. DIODE LASER STUDY OF THE ISOTOPES OF H_3^+......................................15 min.(1:42)

S. C. FOSTER and A.R.W. McKELLAR, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6.

TE3. OBSERVATION OF THE ν_1 FUNDAMENTAL BAND OF H_2D^+............................15 min.(1:59)

TAKAYOSHI AMANO and J.K.G. WATSON, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6.

TE4. SPECTROSCOPIC PROPERTIES OF SMALL MOLECULAR IONS FROM AB INITIO CALCULATIONS...15 min.(2:16)

P. BOTSCHWINA, J. FLESCH, and W. MEYER, Fachbereich Chemie der Universität Kaiserslautern, D-6750 Kaiserslautern, West Germany.

TE5. OBSERVATION OF THE $\nu_2(1\overset{-}{\leftarrow}0^+)$ INVERSION MODE BAND OF H_3O^+ BY HIGH RESOLUTION SPECTROSCOPY..15 min.(2:33)

NATHAN N. HAESE, DI JIA LIU, and TAKESHI OKA, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637.

TE6. DIODE LASER OBSERVATION OF THE ν_3 BAND OF HCO^+............................15 min.(2:50)

S. C. FOSTER, A.R.W. McKELLAR, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6.

Intermission

TE7. THE OBSERVATION OF THE ν_1(NH STRETCH) AND ν_2(CH STRETCH) OF $HCNH^+$..........15 min.(3:25)

R. S. ALTMAN, M. W. CROFTON, and T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637.

TE8. OBSERVATION OF THE ν_1(N-H) BAND OF $DCNH^+$ WITH A DIFFERENCE FREQUENCY LASER..10 min.(3:42)

TAKAYOSHI AMANO, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6.

TE9. INFRARED SPECTRA OF $^4HeH^+$, $^4HeD^+$, $^3HeH^+$ AND $^3HeD^+$........................15 min.(3:54)

M. W. CROFTON, R. S. ALTMAN, N. N. HAESE, and T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637.

TE10. OBSERVATION OF THE $v=1 \leftarrow 0$ AND $2 \leftarrow 1$ INFRARED BANDS OF KH BY DIODE LASER SPECTROSCOPY...15 min.(4:11)

NATHAN N. HAESE, DI JIA LIU, and ROBERT S. ALTMAN, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637.

TE11. SUB-DOPPLER INFRARED LASER SPECTROSCOPY: VIBRATION-INDUCED eqQ IN $^{189}OsO_4$ AND DETERMINATION OF TETRAHEDRAL SPLITTING CONSTANTS IN $^{189}OsO_4$ AND $^{192}OsO_4$...15 min.(4:28)

F. SCAPPINI, Istituto di Spettroscopia Molecolare del C.N.R., Bologna, Italy; J. M. FRYE, T. OKA, Department of Chemistry, University of Chicago, Chicago, Illinois, 60637; and W. A. KREINER, Abteilung fur Physikalische Chemie, Universität of Ulm, Ulm, West Germany.

TE12. THE FLASHLAMP PUMPED HCN GAS LASER..10 min.(4:45)

D. W. ROBINSON, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland, 21218.

TE13. T19 will be presented here (K. G. LUBIC)......................................10 min.(4:57)

TUESDAY, JUNE 12, 1984 -- 1:30 P.M.

Room 1009, Physics Laboratory

Chairman: V. F. KALASINSKY, Department of Chemistry, Mississippi State
University, Mississippi State, Mississippi.

TF1. AN AB-INITIO THEORY OF VIBRATIONAL CIRCULAR DICHROISM......................15 min.(1:30)

P. J. STEPHENS, Department of Chemistry, University of Southern
California, Los Angeles, California, 90089.

TF2. THE VIBRATIONAL OPTICAL ACTIVITY OF TRANS-1,2-DIDEUTERIOCYCLOPROPANE........15 min.(1:47)

M. A. LOWE, G. A. SEGAL, and P. J. STEPHENS, Department of Chemistry,
University of Southern California, Los Angeles, California, 90089.
Permanant address of LOWE: Department of Chemistry, Boston University,
Boston, Massachusetts, 02215.

TF3. THE VIBRATIONAL OPTICAL ACTIVITY OF TRANS-1,2-DIDEUTERIOCYCLOBUTANE.........15 min.(2:04)

M. A. LOWE, G. A. SEGAL, and P. J. STEPHENS, Department of Chemistry,
University of Southern California, Los Angeles, California, 90089.
Permanent address of LOWE: Department of Chemistry, Boston University,
Boston, Massachusetts, 02215.

TF4. THE VIBRATIONAL OPTICAL ACTIVITY OF PROPYLENE OXIDE.........................15 min.(2:21)

M. A. LOWE, R. KAWIECKI, F. DEVLIN, G. A. SEGAL, and P. J. STEPHENS,
Department of Chemistry, University of Southern California, Los Angeles,
California, 90089. Permanent address of LOWE: Department of Chemistry,
Boston University, Boston, Massachusetts, 02215.

TF5. APPLICATION OF VIBRONIC COUPLING FORMALISM TO THE DETERMINATION OF
VIBRATIONAL CIRCULAR DICHROISM INTENSITIES................................15 min.(2:38)

T. B. FREEDMAN and L. A. NAFIE, Department of Chemistry, Syracuse
University, Syracuse, New York, 13210.

Intermission

TF6. VIBRONIC COUPLING FORMALISM OF INFRARED ABSORPTION INTENSITY AND
VIBRATIONAL CIRCULAR DICHROISM..15 min.(3:15)

L. A. NAFIE and T. B. FREEDMAN, Department of Chemistry, Syracuse
University, Syracuse, New York, 13210.

TF7. VIBRATIONAL CIRCULAR DICHROISM OF HYDROCHLORIDES AND SODIUM SALTS OF
AMINO ACIDS...15 min.(3:32)

W. ZUK, J. COLBERT, and L. NAFIE, Department of Chemistry, Syracuse
University, Syracuse, New York, 13210.

TF8. VIBRATIONAL CIRCULAR DICHROISM OF AMINO ACID DERIVATIVES...................15 min.(3:49)

A. C. FARRELL and L. A. NAFIE, Department of Chemistry, Syracuse
University, Syracuse, New York, 13210.

TF9. FOURIER TRANSFORM INFRARED VIBRATIONAL CIRCULAR DICHROISM OF SUGARS AND
NUCLEIC ACIDS...15 min.(4:06)

D. M. BACK and P. L. POLAVARAPU, Department of Chemistry, Vanderbilt
University, Nashville, Tennessee, 37235.

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Chairman Before Intermission: J. P. DEVLIN, Department of Chemistry, Oklahoma State
University, Stillwater, Oklahoma.

Chairman After Intermission: EUGENE R. NIXON, Department of Chemistry and Laboratory
for Research on the Structure of Matter, University of
Pennsylvania, Philadelphia, Pennsylvania.

TG1. LIFETIMES OF SOME LOW-LYING EXCITED ELECTRONIC STATES OF Fe, Co AND Ni ATOMS
IN SOLID INERT GAS MATRICES..10 min.(1:30)

THOMAS A. CELLUCCI and EUGENE R. NIXON, Department of Chemistry and
Laboratory for Research on the Structure of Matter, University of
Pennsylvania, Philadelphia, Pennsylvania, 19104.

TG2. LASER-INDUCED FLUORESCENCE STUDY OF LOW-LYING ELECTRONIC STATES OF Ni ATOMS
IN SOLID INERT GAS MATRICES..15 min.(1:42)

THOMAS A. CELLUCCI and EUGENE R. NIXON, Department of Chemistry and
Laboratory for Research on the Structure of Matter, University of
Pennsylvania, Philadelphia, Pennsylvania, 19104.

TG3. COMPARISON OF THE GROUND-STATE VIBRATIONAL FUNDAMENTALS OF DIATOMIC
MOLECULES IN THE GAS PHASE AND IN INERT SOLID MATRICES......................15 min.(1:59)

MARILYN E. JACOX, Molecular Spectroscopy Division, National Bureau of
Standards, Washington, D.C., 20234.

TG4. THE INFRARED SPECTRA OF INTERMEDIATES IN THE REACTION OF F ATOMS WITH
ACETONITRILE TRAPPED IN SOLID ARGON.......................................15 min.(2:16)

MARILYN E. JACOX, Molecular Spectroscopy Division, National Bureau
of Standards, Washington, D.C., 20234.

TG5. SPECTROSCOPIC INVESTIGATION OF HSNO IN A LOW TEMPERATURE MATRIX.
UV, VIS, AND IR INDUCED ISOMERIZATIONS....................................15 min.(2:33)

R. P. MÜLLER, M. NONELLA, and J. ROBERT HUBER, Physikalisch-Chemisches
Institut der Universität Zürich, CH-8057 Zürich, Switzerland.

TG6. FTIR SPECTRA OF THE HYDROGEN-BONDED COMPLEX WITH PHOSPHINE AND HF IN SOLID
ARGON..15 min.(2:50)

R. T. ARLINGHAUS and L. ANDREWS, Department of Chemistry, University
of Virginia, Charlottesville, Virginia, 22901.

Intermission

TG7. INFRARED SPECTRA OF DEUTERATED ISOTOPOMERS ISOLATED IN H_2O CLATHRATES.......15 min.(3:30)

H. H. RICHARDSON, P. J. WOOLDRIDGE, and J. P. DEVLIN, Department of
Chemistry, Oklahoma State University, Stillwater, Oklahoma, 74078.

TG8. MATRIX SPECTRA OF ION-PAIR SOLVATES, $S_n \cdot Li^+NO_3^-$ ....15 min.(3:47)

G. RITZHAUPT, K. CONSANI, and J. P. DEVLIN, Department of Chemistry,
Oklahoma State University, Stillwater, Oklahoma, 74078.

TG9. INFRARED MATRIX ISOLATION SPECTROSCOPIC STUDIES OF THE COMPLEXES OF
CYCLOPROPANE AND METHYL-SUBSTITUTED CYCLOPROPANES WITH THE HYDROGEN
HALIDES..15 min.(4:04)

CANDACE E. TRUSCOTT and BRUCE S. AULT, Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio, 45221.

TG10. INFRARED MATRIX ISOLATION STUDY OF THE 1:1 COMPLEXES BETWEEN THIONYL
FLUORIDE AND SULFUR TETRAFLUORIDE AND SUBSTITUTED AMINES....................15 min.(4:21)

CRAIG S. SASS and BRUCE S. AULT, Department of Chemistry, University
of Cincinnati, Cincinnati, Ohio, 45221

TUESDAY, JUNE 12, 1984 -- 1:30 P.M.

Room 1008, Evans Chemical Laboratory

Chairman Before Intermission: A. F. WAGNER, Argonne National Laboratory, Argonne,
Illinois.

Chairman After Intermission: C.C.J. ROOTHAAN, Departments of Chemistry and Physics,
University of Chicago, Chicago, Illinois.

A. C. WAHL MEMORIAL SESSION

TH1. GROWTH TO MATURITY OF THE MCSCF MODEL............... (INVITED PAPER)········20 min.(1:30)

> C.C.J. ROOTHAAN, Departments of Chemistry and Physics, University of
> Chicago, Chicago, Illinois, 60637.

TH2. ELECTRONIC STRUCTURE OF THE HELIUM MOLECULAR ANION, He_2^-....................10 min.(1:52)

> H. H. MICHELS, United Technologies Research Center, East Hartford,
> Connecticut, 06108.

TH3. A VARIATION METHOD FOR THE CALCULATION OF DYNAMIC POLARIZABILITIES AND
TWO-PHOTON TRANSITION MOMENTS. THE DRESSED MOLECULE APPROACH...............15 min.(2:04)

> WINIFRED M. HUO, Radiation Laboratory, University of Notre Dame, Notre
> Dame, Indiana, 46556. Mailing address: NASA-Ames Research Center,
> Mail Stop 230-3, Moffett Field, California, 94035.

TH4. ELECTRONIC STRUCTURE OF FeO, RuO, FeH, AND RuH............................15 min.(2:21)

> M. KRAUSS and W. J. STEVENS, Molecular Spectroscopy Division,
> National Bureau of Standards, Washington, D.C., 20234.

TH5. FIELD-THEORETIC METHODS FOR SEPARATED-PAIR BCS FUNCTIONS....................15 min.(2:38)

> J. B. ENGLAND, Department of Chemistry and Laboratory for Surface
> Studies, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin, 53201;
> D. M. SILVER, Applied Physics Laboratory, Johns Hopkins University,
> Laurel, Maryland, 20707; and E. O. STEINBORN, Institut für Physikalische
> und Theoretische Chemie, Universität Regensburg, D-8400 Regensburg,
> West Germany.

TH6. AB INITIO COUPLING COEFFICIENTS BETWEEN THE LOWEST IONIC AND COVALENT
STATES OF KBr_2...15 min.(2:55)

> E. M. GOLDFIELD, E. A. GISLASON, and N. H. SABELLI, Department of
> Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.

Intermission

TH7. MEASURES OF THE SMALL CORE-VALENCE AND CORE-CORE CORRELATION ENERGY ERRORS
IN THE OPTIMIZED VALENCE CONFIGURATIONS (OVC) METHOD OF DAS AND WAHL........10 min.(3:30)

> DANIEL D. KONOWALOW, Department of Chemistry, State University of
> New York at Binghamton, Binghamton, New York, 13901.

TH8. CALCULATION OF RADIATIVE TRANSITION PROBABILITIES IN THE $B^1\Pi_u - X^1\Sigma_g^+$
BANDS OF Li_2 AND Na_2...15 min.(3:42)

> W. T. ZEMKE, Department of Chemistry, Wartburg College, Waverly, Iowa,
> 50677; J. T. BAHNS, W. T. LUH, and W. C. STWALLEY, Iowa Laser Facility
> and Department of Chemistry, University of Iowa, Iowa City, Iowa, 52242.

TH9. COMPUTATIONAL CHEMISTRY AT NASA AMES RESEARCH CENTER: AN ACTIVITY
INITIATED WITH HELP AND INSPIRATION FROM A. C. WAHL........................15 min.(3:59)

> J. O. ARNOLD, Computational Chemistry and Aerothermodynamics Branch,
> NASA-Ames Research Center, Moffett Field, California, 94035.
> (Paper will be presented by WINIFRED M. HUO.)

TH10. ANHARMONIC VIBRATIONAL ANALYSES OF AB INITIO POTENTIAL ENERGY SURFACES
FOR FORMALDEHYDE..10 min.(4:16)

> R. J. WHITEHEAD, Chemistry Division, Argonne National Laboratory,
> Argonne, Illinois, 60439; and R. C. ERMLER, Department of Chemistry
> and Chemical Engineering, Stevens Institute of Technology, Hoboken,
> New Jersey, 07030.

TH11. RELATIVISTIC AND CORRELATION CONTRIBUTIONS TO THE 2s3p SINGLET-TRIPLET
INVERSION IN THE BERYLLIUM ISOELECTRONIC SEQUENCE.........................15 min.(4:28)

> Y.-K. KIM and A. W. WEISS, National Bureau of Standards,
> Washington, D.C., 20234.

TH12. MONTE CARLO LIQUID H_2O SIMULATION WITH 4-BODY INTERACTIONS INCLUDED.........15 min.(4:45)

  JOHN DETRICH, G. CORONGIU, and E. CLEMENTI, IBM Corporation,
  P. O. Box 390, Poughkeepsie, New York, 12602.

TH13. CALCULATED THERMAL AND VIBRATIONALLY EXCITED RATE CONSTANTS FOR
  $O(^3P)+H_2$, D_2, AND HD..10 min.(5:02)

  A. F. WAGNER, Argonne National Laboratory, Argonne, Illinois, 60639;
  J. M. BOWMAN, Illinois Institute of Technology, Chicago, Illinois, 60616;
  and G. C. SCHATZ, Northwestern University, Evanston, Illinois, 60201.

TH14. 17 will be presented here (JAMES F. HARRISON)..............................10 min.(5:14)

WEDNESDAY, JUNE 13, 1984 -- 8:45 A.M.

Auditorium, Independence Hall

CHAIRMAN: K. NARAHARI RAO, Department of Physics,
            The Ohio State University, Columbus, Ohio.

Plenary Session

WA1.   CAN WE DETERMINE THE BARE PAIR POTENTIAL OF H_2
        BY SPECTROSCOPY AT HIGH PRESSURE?...............40 min.

        I. F. SILVERA, Department of Physics,
        Harvard University, Cambridge, Massachusetts,
        02138.

WA2.   INFRARED SPECTROSCOPY USING TUNABLE
        LASER SOURCES...................................40 min.

        TAKESHI OKA, Department of Chemistry,
        The University of Chicago, Chicago,
        Illinois, 60637.

Intermission

WA3.   INFRARED SPECTROSCOPY OF MOLECULAR IONS.........40 min.

        RICHARD J. SAYKALLY, Department of Chemistry,
        University of California, Berkeley, Berkeley,
        California, 94720.

WEDNESDAY, JUNE 13, 1984 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chairman: R. H. TIPPING, Department of Physics, University of Alabama,
University, Alabama.

SEMINAR OF INVITED PAPERS ON HYDROGEN

WE1. COMPARISON BETWEEN THEORY AND EXPERIMENT FOR EXCITED STATES OF MOLECULAR
HYDROGEN..30 min.(1:30)

K. DRESSLER, Physical Chemistry Laboratory, ETH-Zentrum, CH-8092
Zurich, Switzerland.

WE2. SCALAR AND VECTOR COLLISIONAL INTERFERENCE EFFECTS IN THE VIBRATION
ROTATION SPECTRA OF HD AND H_2..30 min.(2:03)

R. M. HERMAN, Department of Physics, Pennsylvania State University,
University Park, Pennsylvania, 16802.

WE3. INTERFERENCE EFFECTS IN THE INFRARED SPECTRUM OF HD.........................25 min.(2:36)

A.R.W. McKELLAR, J.W.C. JOHNS, W. MAJEWSKI, Herzberg Institute of
Astrophysics, National Research Council of Canada, 100 Sussex Drive,
Ottawa, Ontario, Canada, K1A OR6; and N. H. RICH, Department of
Physics, Memorial University of Newfoundland, St. John's,
Newfoundland, Canada, A1B 3X7.

Intermission

WE4. THE PURE ROTATIONAL SPECTRUM OF HD: INTRACOLLISIONAL INTERFERENCE AND
DETERMINATION OF THE PERMANENT DIPOLE MOMENT..............................20 min.(3:15)

G. C. TABISZ, Department of Physics, University of Manitoba, Winnipeg,
Manitoba, Canada, R3T 2N2.

WE5. THE FAR INFRARED SPECTRUM OF H_2 AND H_2 IN MIXTURE WITH He: EXPERIMENT
AND THEORY...30 min.(3:38)

L. FROMMHOLD, Department of Physics, University of Texas at Austin,
Austin, Texas, 78712; and G. BIRNBAUM, National Bureau of Standards,
Washington, D.C., 20234.

WE6. CHARGE INDUCED EFFECTS IN THE SPECTRA OF SOLID DEUTERIUM....................20 min.(4:11)

J. D. POLL, Guelph-Waterloo Program for Graduate Work in Physics,
University of Guelph Campus, Guelph, Ontario, Canada, N1G 2W1.

WE7. COLLISION-INDUCED VIBRATIONAL ABSORPTION IN THE HYDROGENS...................30 min.(4:24)

S. P. REDDY, Department of Physics, Memorial University, St. John's,
Newfoundland, Canada, A1B 3X7.

WEDNESDAY, JUNE 13, 1984 -- 2:15 P.M

Room 1009, Physics Laboratory

Chairperson Before Intermission	B. P. WINNEWISSER, Physikalisch-Chemisches Institut, Justus-Liebig-Universitaet Giessen, D-6300 Giessen, West Germany.
Chairman After Intermission	C. RICHARD QUADE, Department of Physics, Texas Tech University, Lubbock, Texas.

WF1. THEORY FOR VIBRATION-ROTATION-LARGE AMPLITUDE MOTION INTERACTIONS...........15 min.(2:15)

> YUHUA GUAN and C. RICHARD QUADE, Department of Physics, Texas Tech University, Lubbock, Texas, 79409.

WF2. INTERNAL COORDINATE FORMULATION FOR THE VIBRATION-ROTATION ENERGIES OF POLYATOMIC MOLECULES. TETRAHEDRAL AND OCTAHEDRAL SPHERICAL TOP MOLECULES...15 min.(2:32)

> WILLIAM B. CLODIUS and C. RICHARD QUADE, Department of Physics, Texas Tech University, Lubbock, Texas, 79409.

WF3. RELATING ALTERNATIVE FORMULATIONS OF ASYMMETRIC-ROTATOR HAMILTONIANS WRITTEN IN TERMS OF CYLINDRICAL-TENSOR ANGULAR-MOMENTUM OPERATORS...........15 min.(2:49)

> PAUL M. PARKER, Department of Physics, Michigan State University, East Lansing, Michigan, 48824.

WF4. GROUP THEORETICAL TREATMENT OF THE PLANAR INTERNAL ROTATION PROBLEM IN $(HF)_2$...15 min.(3:06)

> JON T. HOUGEN, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C., 20234; and NOBUKIMI OHASHI, Department of Physics, Kanazawa University, Kanazawa, Ishikawa, 920, Japan.

WF5. THE SEMIRIGID BENDER AND INTERNAL ISOMERIZATION OF HCN TO CNH...............10 min.(3:23)

> S. C. ROSS, Department of Chemistry, University of Alberta, Edmonton, (ARRIVED LATE) Alberta, Canada, T6G 2G2.

Intermission

WF6. PREDICTION OF MANY NEW OPTICALLY PUMPED SUBMILLIMETER-WAVE LASER EMISSIONS IN CDF_3...10 min.(3:45)

> J. P. SATTLER, R. P. LEAVITT, T. L. WORCHESKY, and M. S. TOBIN, U. S. ARMY ERADCOM, Harry Diamond Laboratories, Adelphi, Maryland, 20783.

WF7. THE MICROWAVE SPECTRUM OF TRIFLUOROETHYLENE OXIDE...........................10 min.(3:57)

> T. T. RAW and C. W. GILLIES, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, 12181.

WF8. MOLECULAR STRUCTURE OF TRANS-1,2-DIFLUOROCYCLOPROPANE.......................15 min.(4:09)

> N. CRAIG, Department of Chemistry, Oberlin College, Oberlin, Ohio, 44074; C. W. GILLIES, H. JUSTNES, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, 12181; and S. SENGUPTA, Department of Chemistry, Temple University, Philadelphia, Pennsylvania, 19122.

WF9. MICROWAVE SPECTRUM AND MOLECULAR STRUCTURE OF CIS-1,2-DIFLUOROCYCLOPROPANE..15 min.(4:26)

> N. CRAIG, Department of Chemistry, Oberlin College, Oberlin, Ohio, 44074; C. W. GILLIES, H. JUSTNES, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, 12181; and S. SENGUPTA, Department of Chemistry, Temple University, Philadelphia, Pennsylvania, 19122.

WF10. MICROWAVE SPECTRA AND MOLECULAR STRUCTURE OF CIS, TRANS-1,2,3-TRIFLUOROCYCLOPROPANE. ....15 min.(4:43)

> R. N. BEAUCHAMP, C. W. GILLIES, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, 12181; and J. W. AGOPOVICH, Charles Stark Draper Laboratory, Incorporated, 55 Technology Square, Cambridge, Massachusetts, 02139.

WEDNESDAY, JUNE 13, 1984 -- 2:15 P.M.

Room 1005, Physics Laboratory

Chairman: J. E. KENNY, Pearson Chemical Laboratories, Department of Chemistry, Tufts University, Medford, Massachusetts.

WG1. TRANSITION-METAL DIATOMICS: ScNi, TiCo, TiV, VNi.........................15 min.(2:15)

      R. J. VAN ZEE and W. WELTNER, JR., Department of Chemistry, University of Florida, Gainesville, Florida, 32611.

WG2. LiCr AND NaCr MOLECULES...10 min.(2:32)

      R. J. VAN ZEE, W. WELTNER, JR., Department of Chemistry, University of Florida, Gainesville, Florida, 32611; and C. A. BAUMANN, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

WG3. THE GENERATION AND TRAPPING OF HIGH TEMPERATURE CATION RADICALS IN NEON MATRICES AT 4 K: ESR AND AB INITIO CI INVESTIGATION OF $^{28}SiO^+$..............10 min.(2:44)

      LON B. KNIGHT, JR., ANDREW LIGON, Department of Chemistry, Furman University, Greenville, South Carolina, 29613: E. R. DAVIDSON, and DAVID FELLER, JR., Department of Chemistry, University of Washington, Seattle, Washington, 98195.

WG4. ESR SPECTRA OF MATRIX ISOLATED LiO_2.....................................15 min.(2:56)

      D. A. GARLAND and D. M. LINDSAY, Department of Chemistry, City University of New York, The City College, New York, New York, 10031.

WG5. NONPHOTOCHEMICAL HOLE BURNING, SITE INTERCONVERSION AND ISOSBESTIC BEHAVIOUR OF RESORUFIN IN PMMA...15 min.(3:13)

      A. F. CHILDS and A. H. FRANCIS, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

WEDNESDAY, JUNE 13, 1984 -- 3:40 P.M.

Room 1005, Physics Laboratory

Chairman: J. E. KENNY, Pearson Chemical Laboratories, Department of Chemistry, Tufts University, Medford, Massachusetts.

WG'1. MECHANISMS AND RATE CONSTANTS FOR THE VIBRATIONAL RELAXATION OF HD($v = 4,5$, and 6) IN COLLISIONS WITH HD, He, AND D_2.......................15 min.(3:40)

      J. GELFAND, R. B. MILES, Applied Physics & Materials Laboratory, Department of Mechanical & Aerospace Engineering, Princeton University, Princeton, New Jersey, 08544; E. A. ROHLFING, Los Alamos National Laboratory, Group CHM-4, Mail Stop J567, Los Alamos, New Mexico, 87544; and H. RABITZ, Department of Chemistry, Princeton University, Princeton, New Jersey, 08544.

WG'2. ENERGY TRANSFER PATHWAYS FOR $A^2\triangle$ CH IN AN ATMOSPHERIC PRESSURE FLAME........15 min.(3:57)

      NANCY L. GARLAND and DAVID R. CROSLEY, Molecular Physics Department, SRI International, Menlo Park, California, 94025.

WG'3. ROTATIONAL-STATE SPECIFIC ELECTRONIC QUENCHING OF OH($A^2\Sigma^+$, v'=0)...........15 min.(4:14)

      RICHARD A. COPELAND, MARK J. DYER, and DAVID R. CROSLEY, Molecular Physics Department, SRI International, Menlo Park, California, 94025.

WG'4. INTERSYSTEM COLLISIONAL TRANSFER OF EXCITATION AMONG THE TRIPLET STATES OF MOLECULAR NITROGEN...15 min.(4:31)

      W. BENESCH, Institute for Physical Science and Technology, University of Maryland, College Park, Maryland, 20742; and D. FRAEDRICH, Sachs Freeman Associates, 14300 Gallant Fox Lane, Suite 214, Bowie, Maryland, 20715.

WG'5. T11 will be presented here (P. J. WOLF)....................................10 min.(4:48)

WG'6. T12 will be presented here (P. J. WOLF)....................................10 min.(5:00)

WEDNESDAY, JUNE 13, 1984 -- 2:30 P.M.

Room 1008, Evans Chemical Laboratory

Chairman: RUSSELL PITZER, Department of Chemistry, The Ohio State University, Columbus, Ohio.

WH1. EFFECTIVE HAMILTONIANS IN FOCK SPACE AND THE SIMULTANEOUS CALCULATION OF SEVERAL ELECTRONIC STATES......................INVITED PAPER.............30 min.(2.30)

W. KUTZELNIGG and S. KOCH, Lehrstuhl fur Theoretische Chemie, Ruhr-Universität, D-4630 Bochum, Germany.

WH2. NUMERICAL WAVEFUNCTIONS - METHODS FOR THEIR CALCULATION.....INVITED PAPER....30 min.(3.05)

J. HINZE, Fakultät für Chemie, Universität Bielefeld, D 4800 Bielefeld, West Germany.

WH3. AB INITIO CALCULATIONS INCLUDING RELATIVISTIC EFFECTS FOR THE NEUTRAL AND POSITIVE ION DIMERS OF GOLD AND SILVER................................15 min.(3:40)

R. B. ROSS and W. C. ERMLER, Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey, 07030.

WH4. OPTO-VIBRONIC INDUCTION OF CHIRALITY AND SPIN SELECTION RULE IN JAHN-TELLER EFFECT...15 min.(3:57)

YING-NAN CHIU, Center for Molecular Dynamics and Energy Transfer, Department of Chemistry, The Catholic University of America, Washington, D.C., 20064.

WH5 OPTICAL ACTIVITY OF METASTABLE TWISTED ALLENES............................15 min.(4:14)

YING-NAN CHIU, Center for Molecular Dynamics and Energy Transfer, Department of Chemistry, The Catholic University of America, Washington, D.C., 20064.

WH6. THE ELECTRONIC STRUCTURE OF C_4..15 min.(4:31)

Z. Z. WANG, R. N. DIFFENDERFER, and I. SHAVITT, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210. Permanent address for WANG: Institute of Theoretical Chemistry, Jilin University, Changchun, China.

WH7. CALCULATION OF THE POTENTIAL ENERGY CURVES FOR THE LOWEST LYING ELECTRONIC STATES OF THE ISOVALENT DIATOMIC MOLECULES Si_2, Ge_2, SiC AND GeC USING AB INITIO HF-CI METHOD..10 min.(4:48)

IRENE SHIM, K. A. GINGERICH, Department of Chemistry, Texas A&M University, College Station, Texas, 77843; and H. M. NAGARATHNA (NAIK), Department of Physics, University of Wisconsin-Platteville, Wisconsin, 53818.

WH8. 18 will be presented here (M.R.A. BLOMBERG)................................10 min.(5:00)

THURSDAY, JUNE 14, 1984 -- 8:30 A.M.

Room 1153, Physics Laboratory

COBLENTZ PRIZE* AND ASSOCIATED SEMINAR OF INVITED SPEAKERS

Chairman: W. C. LINEBERGER, Department of Chemistry,
           University of Colorado, Boulder, Colorado.

Award of the Prize by the Coblentz Society to S. R. Leone   (8:30)

RA1. SPECTROSCOPIC INVESTIGATIONS OF MOLECULAR REACTION DYNAMICS (AWARD LECTURE) 40 min.(8:40)

          STEPHEN R. LEONE, Joint Institute for Laboratory Astrophysics,
          and Department of Chemistry, University of Colorado; and
          National Bureau of Standards, Boulder, Colorado, 80309.

RA2. VIBRATIONAL STATE-DEPENDENT HYPERFINE COUPLING OF HF..........................30 min.(9:25)

          CH. BREANT, T. BAER, D. NESBITT, and J. L. HALL,
          Joint Institute for Laboratory Astrophysics,
          University of Colorado; and National Bureau of Standards,
          Boulder, Colorado, 80309.

Intermission

RA3. ULTRA SENSITIVE IR LASER ABSORPTION SPECTROSCOPY OF TRANSIENT
      RADICALS AND IONS...30 min.(10:15)

          D. J. NESBITT, H. PETEK, C. GUDEMAN, R. J. SAYKALLY,
          and C. BRADLEY MOORE, Department of Chemistry, University of
          California, Berkeley, California, 94720; and P. R. OGILBY,
          Department of Chemistry, University of New Mexico, Albuquerque,
          New Mexico, 87131.

RA4. OBSERVATIONS OF INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION DYNAMICS
      IN S_1 AROMATICS..30 min.(10:50)

          K. W. HOLTZCLAW, C. S. PARMENTER, and B. M. STONE,
          Department of Chemistry, Indiana University, Bloomington,
          Indiana, 47405.

RA5. ROVIBRONIC ENERGY SURFACES AND SEMI-CLASSICAL DYNAMICS OF POLYATOMIC
      MOLECULES..20 min.(11:25)

          WILLIAM G. HARTER, Theoretical Division T-12, MS-J569
          Los Alamos National Laboratory, Los Alamos, New Mexico,
          87545.

RA6. π21 will be presented here (J. RYCHLEWSKI)..................................10 min.(11:50)

THURSDAY, JUNE 14, 1984 -- 9:30 A M

Room 1009, Physics Laboratory

Chairman: L. S. ROTHMAN, Optical Physics Division, Air Force Geophysics Laboratory,
Hanscom Air Force Base, Bedford, Massachusetts.

RB1. DIFFERENCE FREQUENCY SPECTROSCOPY OF THE FUNDAMENTAL BAND OF $CH(X^2\Pi)$.........15 min.(9:30)

K. G. LUBIC and T. AMANO, Herzberg Institute of Astrophysics,
National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario,
Canada, K1A OR6.

RB2. HIGH RESOLUTION SPECTRUM OF THE HCl DIMER................................ . ...15 min.(9:47)

N. OHASHI and A. S. PINE, Molecular Spectroscopy Division, National
Bureau of Standards, Washington, D.C., 20234.

RB3. SUB-DOPPLER LASER STARK SPECTRA OF THE ν_3 BAND OF FORMIC ACID...............10 min.(10:04)

W. H. WEBER and P. D. MAKER, Physics Department, Research Staff,
Ford Motor Company, Dearborn, Michigan, 48121.

RB4. HIGH RESOLUTION SPECTROSCOPY OF JET-COOLED PROPYNE BY DIRECT INFRARED
ABSORPTION...10 min.(10:16)

J. WANNA and D. S. PERRY, Department of Chemistry, University of
Rochester, Rochester, New York, 14627.

RB5. FAR INFRARED SPECTRA OF H_2O...10 min.(10:28)

J.W.C. JOHNS, Herzberg Institute of Astrophysics, National Research
Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6.

RB6. THE ν_6 BAND OF C_3O_2...10 min.(10:40)

P. JENSEN, Physikalische-Chemisches Institut, Justus Liebig Universität,
D-6300 Giessen, West Germany; and J.W.C. JOHNS, Herzberg Institute of
Astrophysics, National Research Council of Canada, 100 Sussex Drive,
Ottawa, Ontario, Canada, K1A OR6.

RB7. HIGH RESOLUTION FOURIER TRANSFORM AND DIODE LASER IR SPECTRA OF THE
13.37 MICRON BAND OF PROPANE GAS..10 min.(10:52)

S. J. DAUNT, Department of Chemistry, Concordia University, Montréal,
Quebec, Canada, H3G 1M8; D. C. REUTER, D. E. JENNINGS, Infrared and
Radio Astronomy Branch, NASA-Goddard Space Flight Center, Code 693,
Greenbelt, Maryland, 20771; W. E. BLASS, G. W. HALSEY, Molecular
Spectroscopy Laboratory, Department of Physics & Astronomy, The
University of Tennessee, Knoxville, Tennessee, 37996; and J. W. BRAULT,
Kitt Peak National Observatory, 950 North Cherry Avenue, P.O. Box 26732,
Tucson, Arizona, 85726.

RB8. RAMAN SPECTROSCOPY OF GASES WITH A FOURIER TRANSFORM SPECTROMETER; THE
RO-VIB SPECTRUM OF D_2..10 min.(11:04)

D. E. JENNINGS, Infrared and Radio Astronomy Branch, NASA-Goddard
Space Flight Center, Code 693, Greenbelt, Maryland, 20771; A. WEBER,
National Bureau of Standards, Washington, D.C., 20234; and J. W. BRAULT,
National Solar Observatory, 950 North Cherry Avenue, P.O. Box 26732,
Tucson, Arizona, 85726.

RB9. 0.0025 CM^{-1} RESOLUTION WITH THE KITT PEAK FOURIER TRANSFORM SPECTROMETER.... 5 min.(11:16)

D. E. JENNINGS, Infrared and Radio Astronomy Branch, NASA-Goddard
Space Flight Center, Code 693, Greenbelt, Maryland, 20771; R. HUBBARD,
and J. W. BRAULT, National Solar Observatory, 950 North Cherry Avenue,
P.O. Box 26732, Tucson, Arizona, 85726.

RB10. HIGH RESOLUTION INFRARED SPECTROSCOPY OF THE ν_2 AND ν_4 SILANE BANDS.........10 min.(11:23)

J. J. KEADY, Theoretical Division, T-4 MS B212, Los Alamos National
Laboratory, Los Alamos, New Mexico, 87545; and D. E. JENNINGS,
Infrared and Radio Astronomy Branch, NASA-Goddard Space Flight Center,
Code 693, Greenbelt, Maryland, 20771.

RB11. MEASUREMENT AND ANALYSIS OF THE ν_2 AND ν_4 INFRARED BANDS OF $^{13}CD_4$...........15 min.(11:35)

R. S. McDOWELL, M. I. BUCHWALD, M. S. SOREM, Los Alamos National
Laboratory, Los Alamos, New Mexico, 87545; A. G. ROBIETTE, C. DEELEY,
Department of Chemistry, The University of Reading, Whiteknights,
Reading RG6 2AD, England; and W. A. KREINER, Abteilung für Physikalische
Chemie, Universität Ulm, D-7900 Ulm, West Germany.

THURSDAY, JUNE 14, 1984 -- 9:30 A.M.

Room 1005, Physics Laboratory

Chairman: K. YOSHINO, Harvard College Observatory, Cambridge, Massachusetts.

PLEASE NOTE: Several papers in this session arrived late. We apologize for a
bit of possible inhomogeneity in the subjects covered in this session.

RC1. ELECTRONIC SPECTROSCOPY WITH A BOMEM INTERFEROMETER.........................10 min.(9:30)

> W. S. NEIL, D. A. RAMSAY, and M. VERVLOET, Herzberg Institute of
> Astrophysics, National Research Council of Canada, 100 Sussex Drive,
> Ottawa, Ontario, Canada, K1A OR6.

RC2. EXPERIMENTAL AND THEORETICAL STUDIES OF THE RADIATIVE LIFETIME AND
PREDISSOCIATION RATES OF THE $A^2\Delta$ STATE OF PH^+...............................15 min.(9:42)

> N. ELANDER, P. ERMAN, O. GUSTAFSSON, M. LARSSON, M. RITTBY, Research
> Institute of Physics, S-104 05 Stockholm, Sweden; and E. RURARZ,
> Institute of Nuclear Research, Swierk, 05-400, Poland.

RC3. LASER SPECTROSCOPY OF HOLMIUM AND DYSPROSIUM OXIDES.........................15 min.(9:59)

> C. LINTON, Y. C. LIU, Department of Physics, University of New Brunswick,
> Fredericton, New Brunswick, Canada, E3B 5A3; H. SCHALL, R. W. FIELD,
> Department of Chemistry, Massachusetts Institute of Technology, Cambridge,
> Massachusetts, 02139; and M. DULICK, Air Force Geophysics Laboratory,
> Hanscom Air Force Base, Massachusetts, 01731.

RC4. THE $B^2\Sigma \rightarrow A^2\Pi$ SYSTEM OF SiN...15 min.(10:16)

> S. C. FOSTER, Herzberg Institute of Astrophysics, National Research
> Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6.

RC5. ROTATIONAL AND VIBRATIONAL CONSTANTS OF SEVERAL LOW-LYING LEVELS OF NCO
FROM 4658 Å PUMPED LEF..15 min.(10:33)

> K. N. WONG, A. J. KOTLAR, W. R. ANDERSON, and J. A. VANDERHOFF,
> Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland, 21005.

RC6. ION LASER EXCITATION OF C_2 AND CN FLUORESCENCE IN A FLAME: ASSIGNMENT
OF PUMP TRANSITIONS AND EXCITED STATE ENERGY TRANSFER........................15 min.(10:50)

> K. N. WONG, J. A. VANDERHOFF, W. R. ANDERSON, and A. J. KOTLAR,
> Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland, 21005.

RC7. INTRACAVITY Kr^+ LASER EXCITATION OF NH_2 IN AN NH_3/N_2O FLAME.................15 min.(11:07)

> K. N. WONG, W. R. ANDERSON, J. A. VANDERHOFF, and A. J. KOTLAR,
> Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland, 21005.

RC8. LASER EXCITED FLUORESCENCE STUDIES OF THE PO RADICAL........................15 min.(11:24)

> W. R. ANDERSON, L. J. DECKER, A. J. KOTLAR, and M. A. DEWILDE,
> Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland, 21005.

RC9. ELECTRONIC ENERGY TRANSFER IN N_2^+.....................................10 min.(11:41)

> D. H. KATAYAMA, Ionospheric Physics Division, Air Force Geophysics
> Laboratory, Hanscom Air Force Base, Massachusetts, 01731.

RC10. N20 will be presented here (P. MISRA).......................................10 min.(11:53)

THURSDAY, JUNE 14, 1984 -- 1:00 P.M.

Room 1153, Physics Laboratory

Chairman Before Intermission: JOSEPH P. SATTLER, U.S. Army Electronics Research and Development, Harry Diamond Laboratories, Adelphi, Maryland.

Chairman After Intermission: R. H. SCHWENDEMAN, Department of Chemistry, Michigan State University, East Lansing, Michigan.

RE1. A REVIEW OF RECENT INFRARED WORK ON HYDROGEN-BONDED MOLECULES..............30 min.(1:00)

WALTER J. LAFFERTY, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C., 20234.

INVITED PAPER

RE2. THE H_2S SPECTRUM BETWEEN 2150 AND 2950 CM^{-1}: LINE POSITIONS AND INTENSITIES..15 min.(1:35)

L. LECHUGA-FOSSAT, J.-M. FLAUD, C. CAMY-PEYRET, Laboratoire de Physique Moléculaire et d'Optique Atmosphérique, C.N.R.S., Campus d'Orsay, 91405 Orsay, France.

RE3. FIRST DERIVATIVES OF THE DIPOLE MOMENT OF XY_2 ASYMMETRIC ROTORS: H_2O, NO_2, H_2S......................................15 min.(1:52)

C. CAMY-PEYRET and J.-M. FLAUD, Laboratoire de Physique Moléculaire et d'Optique Atmosphérique, C.N.R.S., Campus d'Orsay, 91405 Orsay, France.

RE4. CALCULATIONS OF ROVIBRATIONAL SPECTRA OF WATER BY MEANS OF PARTICLES-ON-CONCENTRIC-SPHERES...10 min.(2:09)

G. A. NATANSON, R. S. BERRY, Department of Chemistry, University of Chicago, Chicago, Illinois, 60637; G. S. EZRA, Department of Chemistry, Cornell University, Ithaca, New York, 14850; and G. DELGADO-BARRIO, Institute de Estructura de la Materia, C.S.I.C., Madrid-6, Spain.

RE5. INITIAL STUDIES WITH A BOMEM FTIR SPECTROMETER: THE IR SPECTRUM OF C_2N_2....15 min.(2:21)

A. WEBER, W. J. LAFFERTY, and W. B. OLSON, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C., 20234.

RE6. MINIMIZATION OF VOLUME AND ASTIGMATISM OF WHITE-TYPE MULTIPLE REFLECTION ABSORPTION CELLS FOR USE WITH CIRCULAR OR SQUARE APERTURES AND IMAGES.......15 min.(2:39)

W. B. OLSON, Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C., 20234.

RE7. INFRARED INTENSITIES OF SMALL POLYATOMIC MOLECULES CALCULATED FROM CEPA DIPOLE MOMENT FUNCTIONS AND ANHARMONIC VIBRATIONAL WAVEFUNCTIONS............10 min.(2:56)

P. BOTSCHWINA, Fachbereich Chemie der Universität Kaiserslautern, D-6750 Kaiserslautern, West Germany.

Intermission

RE8. ABSORPTIONS OF NH_3, CO_2, H_2O, N_2O, AND CH_4 AS INFRARED CALIBRATION STANDARDS: COMPARISON OF ABSOLUTE ACCURACIES..............................10 min.(3:25)

LINDA R. BROWN and ROBERT A. TOTH, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91109.

RE9. SATURATION LAMB DIP SPECTROSCOPY USING MICROWAVE MODULATION SIDEBANDS ON CO_2 LASER LINES: THE ν_2 BAND OF AMMONIA....................................15 min.(3:37)

G. MAGERL, W. SCHUPITA, Institut für Nachrichtentechnik, Technical University of Vienna, Vienna, Austria; J. M. FRYE, T. OKA, Department of Chemistry, University of Chicago, Chicago, Illinois, 60637; and W. A. KREINER, Abteilung für Physikalische Chemie, University of Ulm, Ulm, West Germany.

RE10. THE ν_2 SPECTRUM OF NH_3..10 min.(3:54)

R. L. POYNTER and JACK S. MARGOLIS, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91109.

RE11. USE OF LONG-PATH FOURIER TRANSFORM INFRARED SPECTRA FROM KITT PEAK IN THE STUDY OF AMMONIA...15 min.(4:06)

Š. URBAN, R. D'CUNHA, JON MANHEIM, and K. NARAHARI RAO, Department of Physics, The Ohio State University, Columbus, Ohio, 43210. Permanant address of MANHEIM: Wright Patterson Air Force Base, Ohio, 45433.

RE12. SPECTRUM OF THE ν_2 BAND OF $^{15}NH_3$ WITH A PRECISION BETTER THAN 0.0005 CM^{-1}...10 min.(4:23)

L. HENRY, A. VALENTIN, Laboratoire de Spectronomie Moléculaire,
Université Pierre et Marie Curie, 75230 Paris, France; R. D'CUNHA,
Š. URBAN, and K. NARAHARI RAO, Department of Physics, The Ohio
State University, Columbus, Ohio, 43210.

RE13. THE ANALYSIS OF THE $\nu_1 + \nu_2$ AND $\nu_1 + \nu_2 - \nu_2$ BANDS OF $^{14}NH_3$ AND $^{15}NH_3$........10 min.(4:35)

Š. URBAN, P. MISRA, R. D'CUNHA, and K. NARAHARI RAO, Department of
Physics, The Ohio State University, Columbus, Ohio 43210.

RE14. ENERGY LEVELS OF AMMONIA..10 min.(4:47)

Š. URBAN, R. D'CUNHA, K. NARAHARI RAO, Department of Physics, The
Ohio State University, Columbus, Ohio, 43210; and D. PAPOUSEK,
The J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, Prague, Czechoslovakia.

THURSDAY, JUNE 14, 1984 -- 1:00 P.M.

Room 1009, Physics Laboratory

Chairman Before Intermission: W. R. ANDERSON, Ballistic Research Laboratory,
Aberdeen Proving Ground, Maryland.

Chairman After Intermission: D. L. HUESTIS, Molecular Physics Department,
SRI International, Menlo Park, California.

RF1. THE $\tilde{A}^1A''$ EXCITED ELECTRONIC STATE OF HCN: ISOTOPIC EVIDENCE THAT UNIFIES EXPERIMENT AND THEORY..15 min.(1:00)

> G. A. BICKEL and K. K. INNES, Department of Chemistry, State University of New York at Binghamton, Binghamton, New York, 13901.

RF2. FLUORESCENCE MEASUREMENTS ON HCP...15 min.(1:17)

> KEVIN K. LEHMANN, The Society of Fellows and Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

RF3. INFRARED EMISSION SPECTRA OF NH_2..10 min.(1:34)

> M. VERVLOET, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6.

RF4. MICROWAVE-OPTICAL DOUBLE RESONANCE OF HNO AND DNO IN THE $\tilde{A}^1A''$(000) STATE....15 min.(1:46)

> J. C. PETERSEN, T. AMANO, D. A. RAMSAY, Herzberg Institute of Astro-Physics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6; and S. SAITO, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan.

RF5. LASER-INDUCED FLUORESCENCE MEASUREMENT OF SPIN-ORBIT SPLITTINGS IN EXCITED VIBRATIONAL LEVELS OF $NCO(X^2\Pi_i)$....................................15 min.(2:03)

> RICHARD A. COPELAND and DAVID R. CROSLEY, Molecular Physics Department, SRI International, Menlo Park, California, 94025.

RF6. SPECTROSCOPY OF Cs_3^+...10 min.(2:20)

> H. HELM, R. MÖLLER, K. STEPHAN, P. C. COSBY, and D. L. HUESTIS, Molecular Physics Department, SRI International, Menlo Park, California, 94025.

RF7. ASSIGNMENT OF THE $3p^2F_2 - 3s^2A_1$ ELECTRONIC TRANSITION OF ND_4................20 min.(2:32)

> JAMES K.G. WATSON, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6.

Intermission

RF8. CS_2 CONTINUUM - LIKE EMISSION...10 min.(3:10)

> Y. S. LEE and S. J. SILVERS, Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia, 23284.

RF9. HIGH RESOLUTION ABSORPTION CROSS SECTIONS OF OXYGEN IN THE REGION 193-204 nm OF THE SCHUMANN-RUNGE BANDS AND HERZBERG CONTINUUM...............15 min.(3:22)

> A.S.C. CHEUNG, K. YOSHINO, D. E. FREEMAN, and W. H. PARKINSON, Harvard College Observatory, 60 Garden Street, Cambridge, Massachusetts, 02138.

RF10. HIGH RESOLUTION CROSS SECTION MEASUREMENT OF OZONE IN THE WAVELENGTH REGION 240-350 nm..15 min.(3:39)

> D. E. FREEMAN, K. YOSHINO, J. R. ESMOND, and W. H. PARKINSON, Harvard College Observatory, 60 Garden Street, Cambridge, Massachusetts, 02138.

RF11. HIGH RESOLUTION ABSORPTION CROSS SECTION MEASUREMENTS OF SO_2 AT 213 K IN THE WAVELENGTH REGION 172-240 nm...10 min.(3:56)

> K. YOSHINO, D. E. FREEMAN, J. R. ESMOND, and W. H. PARKINSON, Harvard College Observatory, 60 Garden Street, Cambridge, Massachusetts, 02138.

RF12. SPECTROSCOPIC SURVEY OF THE 550 nm REGION OF SUPERSONICALLY COOLED NO_2......15 min.(4:08)

> MENG-CHIH SU and DAVID L. MONTS, Department of Chemistry, University of Arkansas, Fayetteville, Arkansas, 72701.

RF13. MULTI-PHOTON PHOTODISSOCIATION OF XENON DIFLUORIDE..........................15 min.(4:25)

> DAYO ALUGBIN and ALLAN L. SMITH, Department of Chemistry, Drexel University, Philadelphia, Pennsylvania, 19104.

RF14. 714 will be presented here (YEN CHU HSU)..................................10 min.(4:42)

THURSDAY, JUNE 14, 1984 -- 1:00 P.M.

Room 1005, Physics Laboratory

Chairman: P. DUTTA, Department of Chemistry, The Ohio State University, Columbus, Ohio.

RG1. DEVELOPMENT OF A NEW TUNABLE VISIBLE WAVELENGTH NARROW BAND REJECTION
FILTER...15 min.(1:00)

> PERRY L. FLAUGH, STEPHEN E. O'DONNELL, and SANFORD A. ASHER,
> Department of Chemistry, University of Pittsburgh, Pittsburgh,
> Pennsylvania, 15260.

RG2. SURFACE SELECTION RULES FOR SERS: CALCULATIONS AND APPLICATION TO THE
SERS SPECTRUM OF PHTHALAZINE ON Ag..10 min.(1:17)

> M. MOSKOVITS and J. S. SUH, Department of Chemistry and Erindale
> College, University of Toronto, Toronto, Ontario, Canada, M5S 1A1.

RG3. A VAN DER WAALS STATE OF MATRIX-ISOLATED Cr_2.................................15 min.(1:29)

> W. LIMM, M. MOSKOVITS, Department of Chemistry, University of
> Toronto, Toronto, Ontario, Canada, M5S 1A1; and T. MEJEAN,
> Laboratoire de la Spectroscopie Infrarouge, Université de
> Bordeaux I, 33405 Talence, France.

RG4. SURFACE COHERENT RAMAN SCATTERING ON ZnO OPTICAL WAVEGUIDES.................15 min.(1:46)

> W. M. HETHERINGTON, E. W. KOENIG, N. W. VAN WYCK, Department of
> Chemistry, University of Arizona, Tucson, Arizona, 85721;
> R. M. FORTENBERRY, and G. I. STEGEMAN, Optical Sciences Center,
> University of Arizona, Tucson, Arizona, 85721.

RG5. ISOLATED CH STRETCHING MODES IN NORMAL ALKANES: CAN ISOTOPIC SUBSTITUTION
AFFECT CONFORMER POPULATION?..15 min.(2:03)

> W. F. MURPHY, Division of Chemistry, National Research Council of
> Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6.

Intermission

RG6. RESONANCE RAMAN SPECTRA AND EXCITATION PROFILES OF METAL(II)DITHIZONATES....15 min.(2:35)

> D. F. MICHALSKA, Department of Chemistry, Vanderbilt University,
> Nashville, Tennessee, 37235; and A. T. KOWAL, Institute of Inorganic
> Chemistry and Metallurgy of Rare Elements, Technical University,
> Wroclaw, Poland.

RG7. UV RESONANCE RAMAN STUDIES OF AROMATIC AND POLYCYCLIC AROMATIC
HYDROCARBONS...15 min.(2:52)

> SANFORD A. ASHER and CRAIG R. JOHNSON, Department of Chemistry,
> University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

RG8. UV RESONANCE RAMAN STUDIES OF AROMATIC AMINO ACIDS.........................15 min.(3:09)

> M. LUDWIG, T. SMART, C. J. JOHNSON, and S. A. ASHER, Department of
> Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

RG9. OPTICAL STARK EFFECTS IN THE ROTATIONAL-VIBRATIONAL RAMAN SPECTRUM OF O_2....15 min.(3:26)

> R. A. HILL, A. OWYOUNG, and P. ESHERICK, Sandia National Laboratories,
> Albuquerque, New Mexico, 87185.

RG10. PRESSURE DEPENDENCE OF THE STIMULATED RAMAN Q-BRANCH SPECTRUM OF D_2
DILUTED IN He, A, AND N_2..15 min.(3:43)

> G. J. ROSASCO and W. S. HURST, Temperature and Pressure Division,
> Center for Basic Standards, National Bureau of Standards,
> Washington, D.C., 20234.

RG11. $\Sigma 6$ will be presented here (G.N.R. TRIPATHI)................................15 min.(4:00)

RG12. $\Sigma 10$ will be presented here (D. C. SHIEH)....................................15 min.(4:17)

RG13. $\Sigma 20$ will be presented here (G.N.R. TRIPATHI)................................15 min.(4:34)

RG14. $\Sigma 13$ will be presented here (M. H. VAN BENTHEM)..............................10 min.(4:51)

THURSDAY, JUNE 14, 1984 -- 1:00 P.M.

Room 1008, Evans Chemical Laboratory

Chairman: ROBERT L. SWOFFORD, Corporate Research Center, The Standard Oil Company, Warrensville Heights, Ohio.

RH1. THE ELECTRONIC SPECTRA OF HEXATRIENES.......................................15 min.(1:00)

A. SABLJIĆ, R. McDIARMID, Laboratory of Chemical Physics, National Institutes of Health, Building 2, Room B1-07, Bethesda, Maryland, 20205; and J. P. DOERING, Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland, 21218.

RH2. THE $1^1B_u^+ \leftarrow 1^1A_g^-$ ABSORPTION OF JET-COOLED TRANS, TRANS-1,3,5,7-OCTATETRAENE..10 min.(1:17)

M. F. GRANVILLE, Department of Chemistry, University of Connecticut, Storrs, Connecticut, 06268; D. G. LEOPOLD, R. D. PENDLEY, and V. VAIDA, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

RH3. LEVEL ORDERING IN CIS-TRANS ISOMERS OF 2,4,6,8-DECATETRAEN-1-AL AND 2,4,6,8,10-DODECAPENTAEN-1-AL..15 min.(1:29)

M. F. GRANVILLE and H. SHEYBANI, Department of Chemistry, University of Connecticut, Storrs, Connecticut, 06268.

RH4. VIBRATIONALLY RESOLVED OPTICAL SPECTROSCOPY OF CIS,TRANS-1,3,5,7-OCTATETRAENE..15 min.(1:46)

BRYAN E. KOHLER and THOMAS A. SPIGLANIN, Department of Chemistry, Wesleyan University, Middletown, Connecticut, 06457.

RH5. EXCITED SINGLET STATE STRUCTURE AND DYNAMICS OF ISOLATED DIPHENYLPOLYENES...15 min.(2:03)

LOU ANN HELMBROOK, BRYAN E. KOHLER, and THOMAS A. SPIGLANIN, Department of Chemistry, Wesleyan University, Middletown, Connecticut, 06457.

RH6. FLUORESCENCE FROM THE 1^1B_u STATE OF TRANS,TRANS-1,3,5,7-OCTATETRAENE IN A FREE JET..15 min.(2:20)

LOU ANN HELMBROOK, BRYAN E. KOHLER, and IRVIN J. LEVY, Department of Chemistry, Wesleyan University, Middletown, Connecticut, 06457.

RH7. PHOTOCHEMISTRY OF CIS,CIS OCTATETRAENE IN THE CONDENSED PHASE...............15 min.(2:37)

BRYAN E. KOHLER and PRADIP MITRA, Department of Chemistry, Wesleyan University, Middletown, Connecticut, 06457.

Intermission

RH8. LASER FLUORESCENCE STUDY OF CYCLOOCTATRIENE IN A SUPERSONIC EXPANSION.......15 min.(3:10)

LOU ANN HELMBROOK and BRYAN E. KOHLER, Department of Chemistry, Wesleyan University, Middletown, Connecticut, 06457.

RH9. THE ORDER OF EXCITED STATES IN POLYYNES.....................................15 min.(3:27)

BRYAN E. KOHLER, DAVID E. SCHILKE, and THOMAS A. SPIGLANIN, Department of Chemistry, Wesleyan University, Middletown, Connecticut, 06457.

RH10. TWO-PHOTON THERMAL LENSING (TPTL) SPECTROSCOPY OF MONOSUBSTITUTED BENZENES..15 min.(3:44)

J. K. RICE, Department of Chemistry, Wesleyan University, Middletown, Connecticut, 06457; D. S. KLIGER, and R. W. ANDERSON, Natural Science Division, University of California, Santa Cruz, California, 95064.

RH11. ODMR STUDIES OF THE PHOSPHORESCENT TRIPLET STATE OF DIHALONAPHTHALENES......10 min.(4:01)

A. M. NISHIMURA, Department of Chemistry, Westmont College, Santa Barbara, California, 93108.

RH12. RESONANCE RAMAN SPECTRA OF THE GROUND AND LOW-LYING EXCITED ELECTRONIC STATES OF Ru(II) PENTAAMMINE PYRIDINE DERIVATIVES...........................15 min.(4:13)

Y. C. CHUNG, N. LEVENTIS, P. J. WAGNER, and G. E. LEROI, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.

RH13. CHARACTERIZATION OF ELECTRONIC STATES OF MIXED-LIGAND Ru(II) ORGANOMETALLIC COMPLEXES BY RESONANCE RAMAN SPECTROSCOPY...................................15 min.(4:30)

Y. C. CHUNG, N. LEVENTIS, P. J. WAGNER, and G. E. LEROI, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.

RH14. 3 will be presented here (GILBERT M. NATHANSON)............................10 min.(4:47)

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FRIDAY, JUNE 15, 1984 -- 8:30 A.M.

Room 1153, Physics Laboratory

Chairman: YASUKI ENDO, Institute for Molecular Science, Okazaki, Japan

FA1. INFRARED-ZERO-FREQUENCY DOUBLE RESONANCE IN A RESONANT D.C. STARK FIELD.....10 min.(8:30)

  SANG LEE, A. JACQUES, and R. H. SCHWENDEMAN, Department of Chemistry,
  Michigan State University, East Lansing, Michigan, 48824.

FA2. MICROWAVE-MICROWAVE FOUR-LEVEL DOUBLE RESONANCE IN NH_3-He AND NH_3-H_2
GAS MIXTURES...10 min.(8:42)

  D. B. PETERSON and R. H. SCHWENDEMAN, Department of Chemistry, Michigan
  State University, East Lansing, Michigan, 48824.

FA3. HIGH RESOLUTION FOURIER TRANSFORM SPECTROSCOPY OF THE v_3, v_4, AND
v_6 BANDS OF D_2CO...15 min.(8:54)

  K. NAKAGAWA, Department of Physics, Toyama University, Toyama 930,
  Japan; R. H. SCHWENDEMAN, Department of Chemistry, Michigan State
  University, East Lansing, Michigan, 48824; and J.W.C. JOHNS,
  Herzberg Institute of Astrophysics, National Research Council of
  Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6.

FA4. SATURATION LASER STARK AND LASER MICROWAVE DOUBLE RESONANCE SPECTROSCOPY
OF OCS INSIDE A CO_2 LASER CAVITY...10 min.(9:11)

  J.-G. LAHAYE, W. K. AHMED, and A. FAYT, Molecular Spectroscopy
  Laboratory, University of Louvain, B1348 Louvain la Neuve, Belgium.

FA5. CO_2 AND CO LASER MICROWAVE DOUBLE RESONANCE SPECTROSCOPY OF OCS. PRECISE
MEASUREMENT OF DIPOLE MOMENT AND POLARIZABILITY ANISOTROPY..................15 min.(9:23)

  KEIICHI TANAKA, HAJIME ITO, KENSUKE HARADA, and TAKEHIKO TANAKA,
  Department of Chemistry, Faculty of Science, Kyushu University 33,
  Hakozaki, Higashiku, Fukuoka 812, Japan.

FA6. CO_2 LASER-MICROWAVE DOUBLE RESONANCE SPECTROSCOPY AND STARK LAMB-DIP
SPECTROSCOPY OF THE v_5 BAND OF CDF_3......................................15 min.(9:40)

  KENSUKE HARADA, MAKOTO HATANAKA, AKIRA INAYOSHI, KEIICHI TANAKA, and
  TAKEHIKO TANAKA, Department of Chemistry, Faculty of Science, Kyushu
  University 33, Hakozaki, Higashiku, Fukuoka 812, Japan.

Intermission

FA7. DIPOLE MOMENT FUNCTION OF OCS...15 min.(10:10)

  KEIICHI TANAKA, TAKEHIKO TANAKA, Department of Chemistry, Faculty of
  Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812, Japan;
  and ISAO SUZUKI, Institute of Information Science, University of Tsukuba,
  Sakuramura, Niihari-gun Ibaraki 300-31, Japan.

FA8. THE TWO-DIMENSIONAL POTENTIAL ENERGY SURFACE FOR THE RING-PUCKERING AND
RING-TWISTING OF 1-SILACYCLOPENT-3-ENE-d_o, 1-d_1, AND 1,1-d_2..............15 min.(10:27)

  J. LAANE and P. M. KILLOUGH, Department of Chemistry, Texas A&M
  University, College Station, Texas, 77843.

FA9. LOW-FREQUENCY VIBRATIONAL SPECTRA AND RING-PUCKERING POTENTIAL ENERGY
FUNCTION OF 2-PHOSPHOLENE AND 2-PHOSPHOLENE-1-d_1............................15 min.(10:44)

  J. LAANE, L. RICHARDSON, J. R. VILLARREAL, and M. A. HARTHCOCK,
  Department of Chemistry, Texas A&M University, College Station,
  Texas, 77843.

FA10. COLLISION-BROADENING PARAMETERS OF ETHANE USING TUNABLE DIODE LASER
TECHNIQUES..5 min.(11:01)

  G. W. HALSEY, Infrared and Radio Astronomy Branch, NASA Goddard Space
  Flight Center, Code 693, Greenbelt, Maryland, 20771; and W. E. BLASS,
  Department of Physics and Astronomy, University of Tennessee, Knoxville,
  Tennessee, 37996.

FA11. HOT BAND INTENSITIES IN THE v_9 REGION OF ETHANE USING TUNABLE DIODE LASER
SPECTROSCOPY..15 min.(11:08)

  G. W. HALSEY, D. E. JENNINGS, Infrared and Radio Astronomy Branch,
  NASA Goddard Space Flight Center, Code 693, Greenbelt, Maryland, 20771;
  and W. E. BLASS, Department of Physics and Astronomy, University of
  Tennessee, Knoxville, Tennessee, 37996.

FA12. THE TORSIONAL GROUND STATE HOT BANDS OF ν_9 OF ETHANE......................15 min.(11:25)

W. E. BLASS, A. A. ATAKAN, Department of Physics and
Astronomy, University of Tennessee, Knoxville, Tennessee,
37996-1200; G. W. HALSEY, D. E. JENNINGS, D. REUTER,
and J. SUSSKIND, NASA, Goddard Space Flight Center,
Greenbelt, Maryland, 20771.

FA13. INFRARED DOUBLE-RESONANCE SPECTROSCOPY OF $^{13}CD_4$..........................15 min.(11:42)
(ARRIVED LATE)

L. LAUX, B. R. FOY, J. I. STEINFELD, Department of
Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts, 02139; and D. HARRADINE,
Department of Chemistry, University of Texas at
Austin, Austin, Texas, 78712.

FA14. Z2 will be presented here (J. M. LISY)...................................10 min.(11:59)

FA15. Z4 will be presented here (F. HERLEMONT)................................10 min.(12:11)

FA16. Z8 will be presented here (RONALD C. CARLSON)...........................10 min.(12:23)

FRIDAY, JUNE 15, 1984 -- 8:30 A.M.

Room 1009, Physics Laboratory

Chairman: C. WELDON MATHEWS, Department of Chemistry, The Ohio State University, Columbus, Ohio.

FB1. OBSERVATION OF THE $a^3\Sigma_g^+ - c^3\Pi_u$, $\Delta v = 1$ SEQUENCE BANDS OF H_2 BY DIFFERENCE FREQUENCY LASER SPECTROSCOPY...................................10 min.(8:30)

> TAKAYOSHI AMANO, Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6.

FB2. H_2 ABSORPTION SPECTRUM IN AN RF DISCHARGE...................................15 min.(8:42)

> G. O. BRINK, K. H. KIM, and A. F. SALIN, Department of Physics and Astronomy, State University of New York at Buffalo, Amherst, New York, 14260.

FB3. FREQUENCY MODULATED VISIBLE LASER ABSORPTION MEASUREMENT OF THE HF 4TH OVERTONE...15 min.(8:59)

> B. A. WOODY and L. LYNDS, United Technologies Corporation, Research Center Silver Lane, East Hartford, Connecticut, 06108.

FB4. FOURIER TRANSFORM EMISSION SPECTRUM OF FeO NEAR 1 μm.......................15 min.(9:16)

> A. W. TAYLOR, A. J. MERER, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada, V6T 1Y6; A.S-C. CHEUNG, Harvard College Observatory, Cambridge, Massachusetts, 02138; and NELSON LEE, Department of Chemistry, McGill University, Montreal, Quebec, Canada.

FB5. THE γ-SYSTEM OF $^{14}N^{34}S$...15 min.(9:33)

> K. S. CHANDRASEKHAR, Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada, V8W 2Y2; and T. K. BALASUBRAMANIAN, Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India.

Intermission

FB6. LASER-INDUCED FLUORESCENCE FROM THE $A^2\Delta$, $B^2\Pi$, $C^2\Sigma^+$, AND $G^2\Sigma^-$ STATES OF THE NS RADICAL...15 min.(10:05)

> J. B. JEFFRIES, GREGORY P. SMITH, and DAVID R. CROSLEY, Chemical Physics Laboratory, SRI International, Menlo Park, California, 94025.

FB7. VIBRATIONAL CONSTANTS DERIVED FROM ROTATIONAL DATA: LaO AND YO.............15 min.(10:22)

> CARLOS B. SUAREZ, Department of Physics, University of La Plata, 1900 La Plata, Argentina.

FB8. C7 will be presented here (R. BACIS)..10 min. (10:39)

FB9. C8 will be presented here (R. BACIS)..10 min. (10:51)

FB10. C9 will be presented here (R. BACIS)..10 min. (11:03)

FB11. C11 will be presented here (G. K. CHAWLA)...................................15 min. (11:15)

FB12. C13 will be presented here (R. W. FIELD)....................................15 min. (11:32)

FB13. C18 will be presented here (S. McDONALD)....................................15 min. (11:49)

FB14. C19 will be presented here (V. E. BONDYBEY).................................15 min. (12:06)

FB15. C4 will be presented here (R. F. BARROW)....................................10 min. (12:23)

FB16. C5 will be presented here (MICHAEL C. HEAVEN)...............................10 min. (12:35)

FB17. C9 will be presented here (H. SCHALL)......................................10 min. (12:47)

FB18. C10 will be presented here (C. M. PATHAK)...................................10 min. (12:59)

FB19. C16 will be presented here (C. LINTON).....................................10 min. (1:11)

FRIDAY, JUNE 15, 1984 -- 8:30 A.M.

Room 1005, Physics Laboratory

Chairman: P. JONES, Department of Chemistry, The Ohio State University, Columbus, Ohio.

FC1. HYDROCARBON-WATER INTERACTIONS: ROTATIONAL SPECTRA AND STRUCTURES OF
ETHYLENE-WATER AND ACETYLENE-WATER COMPLEXES...............................15 min.(8:30)

   K. I. PETERSON and W. KLEMPERER, Department of Chemistry, Harvard
   University, Cambridge, Massachusetts, 02138.

FC2. SPECTROSCOPIC CONSTANTS OF AN ATOM-LINEAR MOLECULE COMPLEX WITH A DOUBLE-
MINIMUM POTENTIAL... ....15 min.(8:47)

   F. J. LIN and W. KLEMPERER, Department of Chemistry, Harvard University,
   Cambridge, Massachusetts, 02138.

FC3. ROTATIONAL SPECTROSCOPY AND STRUCTURE OF SEVERAL NH_3 COMPLEXES..............20 min.(9:04)

   G. T. FRASER, D. D. NELSON, JR., K. R. LEOPOLD, and W. KLEMPERER,
   Department of Chemistry, Harvard University, Cambridge, Massachusetts,
   02138.

FC4. DIPOLE MOMENTS OF CALCIUM MONOHALIDES FROM MOLECULAR BEAM LASER-MICROWAVE
DOUBLE RESONANCE SPECTROSCOPY..15 min.(9:26)

   W. E. ERNST, S. KINDT, and T. TÖRRING, Institut für Molekülphysik,
   Freie Universität Berlin, D-1000 Berlin 33, West Germany.

FC5. THE STARK-HYPERFINE SPECTRUM OF HYDROGEN FLUORIDE, V=1......................15 min.(9:43)

   S. M. BASS, R. L. DeLEON, and J. S. MUENTER, Department of Chemistry,
   University of Rochester, Rochester, New York, 14627.

FC6. RADIO FREQUENCY TRANSITIONS IN ACETYLENE-D_2...............................15 min.(10:00)

   R. L. DeLEON and J. S. MUENTER, Department of Chemistry, University of
   Rochester, Rochester, New York, 14627.

Intermission

FC7. C_2^* CHEMILUMINESCENCE FROM OXIDATION OF GAS PHASE CARBON SPECIES
BY MOLECULAR OXYGEN..15 min.(10:30)

   BRIAN G. WICKE, Department of Physical Chemistry, General Motors
   Research Laboratories, Warren, Michigan, 48090.

FC8. INFRARED PREDISSOCIATION SPECTRA OF WATER DIMER IN A SUPERSONIC
MOLECULAR BEAM...10 min.(10:47)

   R. H. PAGE, Y.-R. SHEN, MMRD, Lawrence Berkeley Laboratory and Department
   of Physics, University of California, Berkeley, California, 94720;
   J. G. FREY, and U.-T. LEE, MMRD, Lawrence Berkeley Laboratory and
   Department of Chemistry, University of California, Berkeley, California,
   94720.

FC9. TWO-PHOTON SPECTROSCOPY OF SURFACE SPECIES.................................15 min. (10:59)

   N. E. VAN WYCK, E. W. KOENIG, and W. M. HETHERINGTON, Department of
   Chemistry, University of Arizona, Tucson, Arizona, 85721.

FC10. ROTATIONAL ANALYSIS OF THE $^2A''-^2A''$ ELECTRONIC TRANSITION OF THE
SUPERSONICALLY COOLED VINOXY RADICAL, CH_2CHO..............................15 min. (11:16)

   L. DI MAURO, TERRY A. MILLER, AT&T Bell Laboratories, Murray Hill,
   New Jersey, 07974; M. HEAVEN, Department of Chemistry, Illinois
   Institute of Technology, Chicago, Illinois, 60616.

FC11. LASER SPECTROSCOPY OF SrOH AND CaOH.......................................15 min. (11:33)

   C. BRAZIER, S. KINSEY-NIELSEN, and P. BERNATH, Department of Chemistry,
   University of Arizona, Tucson, Arizona, 85721.

FC12. OBSERVATION OF CALCIUM AND STRONTIUM MONOFORMATES AND RELATED RADICALS......15 min. (11:50)

   C. BRAZIER, S. KINSEY-NIELSEN, and P. BERNATH, Department of Chemistry,
   University of Arizona, Tucson, Arizona, 85721.

FC13. W1 will be presented here (A. ALI)..15 min.(12:07)

FC14. W3 will be presented here (C. W. MICHAEL)..................................10 min.(12:24)

FC15. W5 will be presented here (I. S. CHENG)....................................15 min.(12:36)

FC16. W6 will be presented here (LAMBERTUS VAN DE BURGT).........................10 min.(12:53)

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Chairman: K. K. INNES, Department of Chemistry, State University of New York
at Binghamton, Binghamton, New York.

FD1. MAGNETIC FIELD EFFECTS ON THE HIGH-RESOLUTION LASER-INDUCED FLUORESCENCE
SPECTRA OF THE MOLECULAR EIGENSTATES OF PYRAZINE AND PYRIMIDINE..............15 min.(8:30)

> J. KOMMANDEUR, Laboratory for Physical Chemistry, University of
> Groningen, 9747 AG Groningen, The Netherlands; W. A. MAJEWSKI,
> Herzberg Institute of Astrophysics, National Research Council of
> Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6;
> W. L. MEERTS, Fysisch Laboratorium, Katholieke Universiteit Nijmegen,
> 6525 ED Nijmegen, The Netherlands; and D. W. PRATT, Department of
> Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

FD2. IS PYRIMIDINE AN INTERMEDIATE STATE MOLECULE?...............................15 min.(8:47)

> W. LEO MEERTS, W. UBACHS, Fysisch Laboratorium, Katholieke Universiteit
> Nijmegen, 6525 ED Nijmegen, The Netherlands; W. A. MAJEWSKI, Herzberg
> Institute of Astrophysics, National Research Council of Canada,
> 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6; B. J. VAN DER MEER,
> and K. E. DRABE, Laboratory of Physical Chemistry, University of
> Groningen, 9747 AG Groningen, The Netherlands.

FD3. SINGLET-TRIPLET PERTURBATIONS IN PYRIMIDINE. MAGNETIC FIELD EFFECTS
ON COLLISION-INDUCED INTERSYSTEM CROSSING...................................15 min.(9:04)

> Y. MATSUMOTO and D. W. PRATT, Department of Chemistry, University
> of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

FD4. DIRECT EXCITATION OF TRIPLET STATES IN A SUPERSONIC JET. THE ROTATIONALLY
RESOLVED LASER-INDUCED PHOSPHORESCENCE SPECTRUM OF GLYOXAL...................15 min.(9:21)

> L. H. SPANGLER, Y. MATSUMOTO, and D. W. PRATT, Department of Chemistry,
> University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

FD5. SIMULTANEOUS FLUORESCENCE EXCITATION AND DIRECT ABSORPTION OF JET-COOLED
AZULENE..15 min.(9:38)

> T. M. WOUDENBERG, M. M. CARRABBA, and J. E. KENNY, Pearson Chemical
> Laboratories, Department of Chemistry, Tufts University, Medford,
> Massachusetts, 02155.

FD6. THE LOWEST $n\pi^*$ TRANSITION OF PYRIMIDINE IN A FREE JET EXPANSION.............15 min.(9:55)

> W. R. MOOMAW, Department of Chemistry, Williams College, Williamstown,
> Massachusetts, 01267; M. M. CARRABBA, and J. E. KENNY, Department of
> Chemistry, Tufts University, Medford, Massachusetts, 02155.

FD7. THE EFFECT OF HYDROGEN BONDING ON THE LOWEST $n\pi^*$ TRANSITION OF PYRIMIDINE
IN A SUPERSONIC JET..10 min.(10:12)

> M. M. CARRABBA, J. E. KENNY, Department of Chemistry, Tufts University,
> Medford, Massachusetts, 02155; and W. R. MOOMAW, Department of Chemistry,
> Williams College, Williamstown, Massachusetts, 01267.

Intermission

FD8. GLYOXAL TRIPLET'S SPECTROSCOPY BY ANTICROSSINGS IN STRONG MAGNETIC FIELD....10 min.(10:35)

> P. DUPRE, R. JOST, L. LEVIANDIER, M. LOMBARDI, E. PEBAY-PEYROULA,
> Laboratoire de Spectrométrie Physique, Université Scientifique et
> Medicale de Grenoble, 38402 Saint Martin d'Heres, France; and
> Service National des Champs Intenses, CNRS, 38042 Grenoble, France.

FD9. LASER SPECTROSCOPY OF THE TETRACENE-ARGON VAN DER WAALS COMPLEXES...........15 min.(10:47)

> W. M. VAN HERPEN, W. LEO MEERTS, A. DYMANUS, Fysisch Laboratorium,
> Katholieke Universiteit Nijmegen, 6525 ED Nijmegen, The Netherlands;
> and W. A. MAJEWSKI, Herzberg Institute of Astrophysics, National
> Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada,
> K1A OR6.

FD10. THE ELECTRONIC SPECTRA OF HYDROGEN BONDED CLUSTERS OF TETRAZINE.............15 min.(11:04)

> CHERYL MORTER, DONALD H. LEVY, James Franck Institute and Department of
> Chemistry, University of Chicago, Chicago, Illinois, 60637; CHRISTOPHER
> A. HAYNAM, Lawrence Livermore Laboratory, Livermore, California, 94550;
> and LINDA YOUNG, Argonne National Laboratory, Argonne, Illinois, 60439.

FD11. THE ELECTRONIC SPECTRUM OF PHENYL-TETRAZINE, Ar-PHENYL-TETRAZINE, AND
THE PHENYL-TETRAZINE DIMER..15 min.(11:21)

YOUNG PARK and DONALD H. LEVY, James Franck Institute and Department of
Chemistry, University of Chicago, Chicago, Illinois, 60637.

FD12. IDENTIFICATION OF TORSIONAL TRANSITIONS IN THE SUPERSONIC JET SPECTRUM
OF MONO-METHYL TETRAZINE...15 min.(11:38)

C. J. SELISKAR and M. A. LEUGERS, Department of Chemistry, University
of Cincinnati, Cincinnati, Ohio, 45221.

FD13. TWO-PHOTON FLUORESCENCE EXCITATION SPECTRUM OF BENZOTRIFLUORIDE. ....15 min.(11:55)

S. DORAISWAMY and N. PERIASAMY, Chemical Physics Group, Tata Institute
of Fundamental Research, Colaba, Bombay, India   400 005.

FD14. Z14 will be presented here (G. SCHERER)...................................15 min.(12:12)

FD15. Z15 will be presented here (Y. CHEN)......................................15 min.(12:29)

FD16. Z16 will be presented here (A. ZABLUDOFF).................................15 min.(12:46)

FD17. Z17 will be presented here (P. H. VACCARO)................................15 min.(1:03)

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PLEASE NOTE: First, we are happy to acknowledge the enthusiastic response from spectroscopists around the world by sending a large number of contributed papers. They have been put into the different sessions on March 3rd and 4th, Saturday and Sunday after the deadline of March 1. The papers that arrived on Monday March 5th have been inserted either at the end of sessions or in session RC. The ones that arrived after March 5th are listed below in this Σ session in the order in which they were received here. We are pleased that it was possible to schedule for presentation all these late papers before the program was sent for duplication on March 15th. Against each of these Σ session papers, there is an indication in which session it will be presented. Thank you for your cooperation and understanding.

Σ1. VIBRATIONAL PREDISSOCIATION SPECTROSCOPY OF BINARY COMPLEXES INVOLVING
BENZENE..15 min.(FC)

A. ALI, J. M. LISY, Department of Chemistry, University of Illinois,
Urbana, Illinois, 61801; and M. HADWIGER, Department of Chemistry,
California Institute of Technology, Pasadena, California, 91125.

Σ2. A NEW METHOD FOR GENERATING PULSED, TUNABLE, INFRARED RADIATION.............10 min.(FA)

J. M. LISY and D. W. MICHAEL, Department of Chemistry, University of
Illinois, Urbana, Illinois, 61801.

Σ3. EXPERIMENTAL AND THEORETICAL STUDIES OF HF DIMER............................15 min.(FC)

D. W. MICHAEL, C. E. DYKSTRA, and J. M. LISY, Department of Chemistry,
University of Illinois, Urbana, Illinois, 61801.

Σ4. DOPPLER-FREE TWO-PHOTON SPECTROSCOPY OF SiF_4 WITH A CO_2 WAVEGUIDE LASER.....10 min.(FA)

F. HERLEMONT, M. AZIZI, and J. LEMAIRE, Laboratoire de Spectroscopie
Hertzienne, CNRS, Université des Sciences et Techniques(Lille I),
59655 Villeneuve d'Ascq, France.

Σ5. STIMULATED EMISSION DUE TO K_2 PHOTODISSOCIATION AND K_2-K COLLISIONS
TRANSFER BY TWO-PHOTON PUMPING IN POTASSIUM VAPOR............................15 min.(FC)

Z. G. WANG, L. J. QIN, Y. Q. LIN, and I. S. CHENG, Department of
Physics, East China Normal University, Shanghai, People's Republic
of China.

Σ6. TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY OF DIHALIDE RADICAL ANIONS.......15 min.(RG)

G.N.R. TRIPATHI, R. H. SCHULER, and R. W. FESSENDEN, Radiation
Laboratory and Department of Chemistry, University of Notre Dame,
Notre Dame, Indiana, 46556.

Σ7. THE ATOMIC ORIGIN OF THE ELECTRONIC MOLECULAR STATES FROM THEIR HYPERFINE
STRUCTURE...10 min.(FB)

M. BROYER, R. BACIS, S. CHURASSY, Laboratoire de Spectrométrie Ionique
et Moléculaire, 69622 Villeurbanne, France; and J. P. PIQUE, Laboratoire
de Spectrométrie Physique, Université de Grenoble, F 38042 Saint-Martin-
d'Heres, France.

Σ8. HYPERFINE STRUCTURE IN THE $f(O_g^+)$ IODINE MOLECULAR STATE....................10 min.(FB)

MME A. BOUVIER, R. BACIS, A. BOUVIER, S. CHURASSY, and J. P. PERROT,
Laboratoire de Spectrométrie Ionique et Moléculaire, 69622 Villeurbanne,
France.

Σ9. PRECISE EXPERIMENTAL DETERMINATION OF LONG RANGE PARAMETERS FROM DIATOMIC
MOLECULAR SPECTRA: CASE OF I_2 AND Li_2......................................10 min.(FB)

F. MARTIN, R. BACIS, D. CERNY, S. CHURASSY, Laboratoire de Spectrométrie
Ionique et Moléculaire, 69622 Villeurbanne, France; and J. VERGES,
Laboratoire Aimé Cotton, CNRS, 91405 Orsay, France.

Σ10. STRUCTURAL INVESTIGATION OF SILICATE SPECIES IN ALKALINE AQUEOUS SOLUTIONS
USING RAMAN SPECTROSCOPY..15 min.(RG)

D. C. SHIEH and P. K. DUTTA, Department of Chemistry, The Ohio State
University, Columbus, Ohio, 43210.

Σ11. STUDY OF EXCITED VIBRATIONAL LEVELS OF THE Na_2 $A^1\Sigma_u^+$ STATE USING MODULATED
GAIN SPECTROSCOPY...15 min.(FB)

G. K. CHAWLA, H. J. VEDDER, R. W. FIELD, Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139;
R. BACIS, and S. CHURASSY, Laboratoire de Spectrometrie Ionique et
Moléculaire, Université Claude Bernard(Lyon I), 69622 Villeurbanne,
France.

Σ12. DIRECT OBSERVATION OF ALL QUASIBOUND ENERGY LEVELS AND LIFETIMES IN THE
Na$_2$ B$^1\Pi_u$ STATE BY CW MODULATED GAIN SPECTROSCOPY..............................15 min.(FB)

G. K. CHAWLA, H. J. VEDDER, and R. W. FIELD, Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.

Σ13. PERTURBATION FACILITATED OPTICAL-OPTICAL DOUBLE RESONANCE STUDIES OF THE
Na$_2$ a$^3\Sigma_u^+$, b$^3\Pi_u$, AND TRIPLET-GERADE RYDBERG STATES..........................15 min.(FB)

LI LI, Qinghai Institute of Salt Lake, Xining, Qinghai, People's
Republic of China; S. RICE, and R. W. FIELD, Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.

Σ14. STIMULATED EMISSION PUMPING OF ACETYLENE: EVIDENCE FOR QUANTUM CHAOTIC
BEHAVIOR NEAR 28000 CM^{-1} OF EXCITATION?.................................15 min.(FD)

R. SUNDBERG, E. ABRAMSON, D. IMRE, G. SCHERER, R. W. FIELD, and
J. L. KINSEY, Department of Chemistry, Massachusetts Institute of
Technology, Cambridge, Massachusetts, 02139.

Σ15. STIMULATED EMISSION SPECTROSCOPY OF ACETYLENE: THE $\tilde{X}^1\Sigma_g^+$ STATE AT
10 000-14 000 CM^{-1}..15 min.(FD)

G. SCHERER, Y. CHEN, S. HALLE, J. L. KINSEY, and R. W. FIELD,
Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts, 02139.

Σ16. DIPOLE MOMENTS IN THE OUT-OF-PLANE BENDING LEVELS OF $\tilde{A}^1A_2$
FORMALDEHYDE-h$_2$ AND -d$_2$...15 min.(FD)

A. ZABLUDOFF, P. H. VACCARO, J. L. KINSEY, R. W. FIELD, Department of
Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts,
02139; and M. CARRERA, University of Chicago, Chicago, Illinois, 60637.

Σ17. ROTATIONAL RELAXATION IN THE v$_4$=1 VIBRATIONAL LEVEL OF H$_2$CO $\tilde{A}^1A_2$ BY
TRANSIENT GAIN SPECTROSCOPY...15 min.(FD)

P. H. VACCARO, J. L. KINSEY, R. W. FIELD, Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139;
R. L. REDINGTON, Department of Chemistry, Texas Tech University,
Lubbock, Texas, 79409; and J. SCHMIDT, Huygens Laboratorium,
Rijksuniversiteit Leiden, 2300 RA Leiden, The Netherlands.

Σ18. ELECTRONIC STRUCTURE OF YbO...15 min.(FB)

S. McDONALD, S. RICE, R. W. FIELD, Department of Chemistry and the
George R. Harrison Spectroscopy Laboratory, Massachusetts Institute
of Technology, Cambridge, Massachusetts, 02139; C. LINTON, Department
of Physics, University of New Brunswick, Fredericton, New Brunswick,
Canada, E3B 5A3; and M. DULICK, Ionospheric Physics Division, Air
Force Geophysics Laboratory/LID, Hanscom Air Force Base, Bedford,
Massachusetts, 01731.

Σ19. MATRIX STUDIES OF LARGE MOLECULE DYNAMICS: EFFECT OF METHYL SUBSTITUTION
UPON VIBRATIONAL RELAXATION..15 min.(FB)

V. E. BONDYBEY and P. M. RENTZEPIS, AT&T Bell Laboratories, Murray
Hill, New Jersey, 07974.

Σ20. TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY OF EXCITED TRIPLET STATES OF
DIPHENYLPOLYENES...15 min.(RG)

G.N.R. TRIPATHI, Radiation Laboratory and Department of Chemistry,
University of Notre Dame, Notre Dame, Indiana, 46556.

Π SESSION

The papers that have been received here between March 15 and May 4 have been scheduled in this session. Each of the papers will have ten minutes for presentation. The session in which it will be presented is indicated in parentheses.

Π1. AB INITIO CALCULATION OF HYPERFINE COUPLING CONSTANTS FOR ATOMS AND SMALL RADICALS...(TD)

W. MEYER and J. FLESCH, Department of Chemistry, Universität Kaiserslautern, Pfaffenbergstraße, Postfach 3049, 6750 Kaiserslautern, West Germany.

Π2. H₂O LINE SHAPE USING THE SINGLE PERTURBER APPROXIMATION..............................(MF)

R. W. DAVIES, S. FAHEY, GTE Laboratories, Inc., Waltham, Massachusetts, 02254; and S. A. CLOUGH, Air Force Geophysics Laboratory(OPI), Hanscom Air Force Base, Massachusetts, 01731.

Π2a. A MOLECULAR LINE SHAPE FORMULATION: APPLICATION TO ATMOSPHERIC CONTINUUM..........(MF)

S. A. CLOUGH, F. X. KNEIZYS, Air Force Geophysics Laboratory(OPI), Hanscom Air Force Base, Massachusetts, 01731; R. W. DAVIES, GTE Laboratories, Inc., Waltham, Massachusetts, 02254; and R. H. TIPPING, Department of Physics, University of Alabama, University, Alabama, 35482.

Π3. FLUORESCENCE POLARIZATION MEASUREMENTS CONCERNING THE ROLE OF ROTATION IN INTRAMOLECULAR ENERGY TRANSFER...(RH)

GILBERT M. NATHANSON and GARY M. McCLELLAND, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

Π4. THE DOUBLE-MINIMUM (2) $^1\Sigma_u^+$ STATE OF Na₂...(FB)

J. VERGES, Laboratoire Aimé Cotton, C.N.R.S.II, 91405 Orsay, France; C. EFFANTIN, J. d'INCAN, Laboratoire de Spectrométrie Ionique et Moléculaire, 69622 Villeurbanne, France; D. L. COOPER, and R. F. BARROW, Physical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, England.

Π5. ROTATIONALLY RESOLVED ELECTRONIC SPECTRA FOR URANIUM MONOXIDE......................(FB)

MICHAEL C. HEAVEN, JEAN-PHILIPPE NICOLAI, Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois, 60616; ERIC K. PARKS, and STEVEN J. RILEY, Chemistry Division, Argonne National Laboratory, Argonne, Illinois, 60439.

Π6. LASER INDUCED FLUORESCENCE SPECTRA OF THE Br₂He VAN DER WAALS COMPLEX..............(FC)

LAMBERTUS VAN DE BURGT, JEAN-PHILIPPE NICOLAI, and MICHAEL C. HEAVEN, Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois, 60616.

Π7. THE ROTATIONAL SPECTRUM OF FLUORONIUMYL (HF$^+$)......................................(MG)

D. C. HOVDE, S. E. STRAHAN, D. RAY, R. J. SAYKALLY, Department of Chemistry, University of California, Berkeley, California, 94720; E. SCHÄFER, Zum Pfarrhag 2, 6238 Hofheim 6, West Germany; C. A. FERRARI, Instituto de Fisica, Universidade Estadual de Campinas, UNICAMP, 13100 Campinas, Sao Paulo, Brazil; and K. G. LUBIC, Herzberg Institute for Astrophysics, National Research Council, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6.

Π8. HIGH RESOLUTION MEASUREMENTS OF INFRARED VIBRATION-ROTATION ABSORPTION LINE STRENGTHS AND LINE FREQUENCIES OF THE ν_2 BENDING MODE OF HOCl(g)...................(FA)

RONALD C. CARLSON, ANTHONY T. YOUNG, and HAROLD S. JOHNSTON, Department of Chemistry, University of California, and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California, 94720.

Π9. SUB-DOPPLER ZEEMAN SPECTROSCOPY OF CeO..(FB)

H. SCHALL, J. GRAY, R. W. FIELD, Department of Chemistry, and the George R. Harrison Spectroscopy Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139; M. DULICK, Ionospheric Physics Division, Air Force Geophysics Laboratory/LID, Hanscom Air Force Base, Bedford, Massachusetts, 01731; and C. LINTON, Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada, E3B 5A3.

Π10. EMISSION SPECTRUM OF TeH...(FB)

N. G. DONGRE, B. P. ASTHANA, and C. M. PATHAK, Laser & Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Varanasi 221005, India.

T 11. CONTINUOUS WAVE OPTICALLY PUMPED IF $B^3\pi(0^+) \rightarrow X^1\Sigma(0^+)$ LASER.........................(WG)

S. J. DAVIS, L. HANKO, and P. J. WOLF, Air Force Weapons Laboratory, Short
Wavelength Laser Branch, Kirtland Air Force Base, New Mexico, 87117.

T 12. VIBRATIONAL AND ROTATIONAL ENERGY TRANSFER IN THE $B^3\pi(0^+)$ STATE OF IF..............(WG)

P. J. WOLF, R. F. SHEA, and S. J. DAVIS, Air Force Weapons Laboratory, Short
Wavelength Laser Branch, Kirtland Air Force Base, New Mexico, 87117.

T 13. LASER INDUCED FLUORESCENCE INVESTIGATION OF INTRAMOLECULAR HYDROGEN BONDING
AND EXCITED STATE PROTON TRANSFER IN 1,5-DIHYDROXYANTHRAQUINONE...................(RG)

M. H. VAN BENTHEM, Air Force Weapons Laboratory, Kirtland Air Force
Base, New Mexico, 87117; and G. D. GILLISPIE, Department of Chemistry,
North Dakota State University, Fargo, North Dakota, 58105.

T 14. VUV LASER-INDUCED FLUORESCENCE STUDY OF THE PREDISSOCIATION OF $HCN(\tilde{A}^1A'')$...........(RF)

YEN CHU HSU, MARK A. SMITH, and STEPHEN C. WALLACE, Department of
Chemistry, University of Toronto, Toronto, Ontario, Canada, M5S 1A1.

T 15. VIBRATIONAL-ROTATIONAL CALCULATIONS ON FORMALDEHYDE................................(MH)

B. MAESSEN and M. WOLFSBERG, Department of Chemistry, University of
California, Irvine, California, 92717.

T 16. OBSERVATION AND ANALYSIS OF THE $2^1\Sigma_g^+$ STATE OF $^7Li_2$ AND $^6Li_2$.......................(FB)

R. BACIS, B. BARAKAT, S. CHURASSY, F. MARTIN, Laboratoire de Spectrométrie
Ionique et Moleculaire, Université Claude Bernard-Lyon I, 69622 Villeurbanne,
France; C. LINTON, Department of Physics, University of New Brunswick,
Fredericton, New Brunswick, Canada, E3B 5A3; S. McDONALD, Department of
Chemistry and the George R. Harrison Spectroscopy Laboratory, Massachusetts
Institute of Technology, Cambridge, Massachusetts, 02139; and J. VERGES,
Laboratoire Aimé Cotton, C.N.R.S. II, 91405 Orsay, France.

T 17. THE BONDING, CHARGE DISTRIBUTION AND DIPOLE MOMENT OF THE LOW LYING STATES
OF CH_2Li_2...(TH)

AILEEN ALVARADO and JAMES F. HARRISON, Department of Chemistry, Michigan
State University, East Lansing, Michigan, 48824.

T 18. THEORETICAL ASSIGNMENT OF THE UV SPECTRA OF ALKYL RADICALS.........................(WH)

M.R.A. BLOMBERG, B. LIU, IBM Research Laboratory, San Jose, California,
95193; B. H. LENGSFIELD, III, BRL, Aberdeen Proving Ground, Maryland,
21005; and P.E.M. SIEGBAHN, Institute of Theoretical Physics, University
of Stockholm, Vanadisvägen 9, S-11346 Stockholm, Sweden.

T 19. OBSERVATION OF THE ν_1 BAND OF D_2H^+ BY DIFFERENCE FREQUENCY SPECTROSCOPY............(TE)

K. G. LUBIC and T. AMANO, Herzberg Institute of Astrophysics, National
Research Council, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A OR6.

T 20. PERFORMANCE OF A 300 GROOVES PER MM, 20 CM X 40 CM (8" X 16") BAUSCH AND LOMB
PLANE GRATING IN A 10-M CZERNY-TURNER SYSTEM OPERATING IN THE ULTRAVIOLET REGION...(RC)

C. WELDON MATHEWS, MICHAEL ST. CLAIR, ELMER WILLIAMS, JR., Department of
Chemistry, The Ohio State University, Columbus, Ohio, 43210; BRAD HARE,
P. MISRA, and K. NARAHARI RAO, Department of Physics, The Ohio State
University, Columbus, Ohio, 43210.

T 21. CALCULATED ELECTRIC AND MAGNETIC PROPERTIES FOR EXCITED STATES OF MOLECULAR
HYDROGEN..(RA)

J. RYCHLEWSKI, Department of Chemistry, University of North Carolina,
Chapel Hill, North Carolina, 27514.

ME1.   (1:00)

LARGE SCALE CI CALCULATIONS FOR DIATOMICS   (INVITED PAPER)

R. AHLRICHS

Calculations on diatomics involving second and third row atoms and transition metals have been performed to determine the scope and limitations of present CI methods (and computers). Special emphasis is given to the convergence of selected properties - R_e, D_e, K_e - with respect to increasing basis set size and configuration space, the latter in connection with size concistency problems. It turns out that very large basis sets - up to g functions - are required at least to push errors below the 1% level.

Address of R. Ahlrichs: Institut f. Physikalische Chemie u. Elektrochemie (Theoretische Chemie), Kaiserstr. 12, D-7500 Karlsruhe, West-Germany

ME2.   (1:35)

OPEN CORE DIATOMIC MOLECULES: LASER TECHNIQUES AND HERETICAL MODELS   (INVITED PAPER·

ROBERT FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.

ME3.   (2:10)

DIFFUSE AND INTERFERENCE BANDS IN ALKALI METAL DIMERS

J. T. BAHNS, W. T. LUH, G. PICHLER, A. M. LYYRA, P. D. KLEIBER, S. P. HENEGHAN, A. DECKERT AND W. C. STWALLEY

With the use of ultraviolet and violet single longitudinal mode laser lines from krypton and argon ion lasers, we have obtained diffuse fluorescence spectra of Na_2 (410-460 nm) and of K_2 (520-580 nm) which clearly show overlapping interference and diffuse structure (work on Li_2 (~440-465 nm) is in progress and will also be reported).

Analysis of the Na_2 spectra indicate that the transitions

$$2^1\Sigma_u^+ \text{ (double minimum)} \rightarrow X^1\Sigma_g^+$$
$$\text{and } 2^3\Pi_g \rightarrow a^3\Sigma_u^+$$
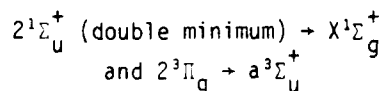
occur in the same spectral region. This overlapping was previously predicted[1] to occur in the case of Li_2. This interpretation is further supported by direct excitation studies of these bands which will also be reported. It might be noted that similar continua have been observed and assigned in Rb_2 and Cs_2. In the former case[2], there is only slight overlap while in the latter case[3], they are well separated.

[1] G. Pichler, S. Milošević, D. Veža and D. D. Konowalow, Chem. Phys. Letters 103, 352 (1984).

[2] G. Pichler, S. Milošević, D. Veža and D. Vukičević, J. Phys. B 16, 4633 (1983).

[3] J. Tellinghuisen, G. Pichler, W. L. Snow, M. E. Hillard and R. J. Exton, Chem. Phys. 50, 313 (1980).

Address of Bahns, Luh, Lyyra, Kleiber, Heneghan and Stwalley: Iowa Laser Facility and Department of Chemistry, University of Iowa, Iowa City, Iowa 52242.
Address of Pichler: Institute of Physics, University of Zagreb, P. O. Box 304, 41001 Zagreb, Yugoslavia.
Address of Deckert: Bethel College, North Newton, Kansas 67117.

ME4.   (2:32)

NEW OPTICALLY-PUMPED LASERS IN THE $B^1\Sigma_u^+ - X^1\Sigma_g^+$ AND $A^1\Sigma_u^+ - X^1\Sigma_g^+$ Bands of Li_2

W. T. LUH, J. T. BAHNS AND W. C. STWALLEY

Many new optically-pumped laser (OPL) lines are obtained from the $^6Li_2$, $^6Li^7Li$ and $^7Li_2$ molecules. These molecules are pumped with krypton ion or argon ion lasers which are operated in a single longitudinal mode. Multiline laser oscillation is obtained in a ring cavity similar to previous work[1,2].

The assignment of the OPL lines within the B-X and A-X bands is done either with the known molecular constants or through the comparison with the assigned laser-induced fluorescence spectra. Calculations of the radiative transition probabilities show excellent correspondence with the observed laser transitions.

[1] A. Rajaei-Rizi, J. T. Bahns, K. K. Verma and W. C. Stwalley, Appl. Phys. Letters 40, 869 (1982).

[2] J. T. Bahns, K. K. Verma, A. R. Rajaei-Rizi and W. C. Stwalley, Appl. Phys. Letters 42, 336 (1983).

Address of Luh, Bahns and Stwalley: Iowa Laser Facility and Department of Chemistry, University of Iowa, Iowa City, Iowa 52242.

ME5.   (2:44)

LASER SPECTROSCOPY OF THE DOUBLE MINIMUM POTENTIAL IN THE $E^1\Sigma_g^+$ STATE OF Li_2

R. A. BERNHEIM, L. P. GOLD, AND C. A. TOMCZYK

Previous work in this laboratory[1] characterized the $E^1\Sigma_g^+$ state of Li_2 (v=0-12) and gave an indication of the possibility of the existence of a double minimum potential in this state. A shallow outer minimum near v=12 was also predicted by an ab initio calculation.[2]

The present work extends the measurements through v=18. Several low J levels from v=13 and 14 exist in the inner minimum portion of the potential with the remaining levels above the barrier showing a sudden dramatic increase in internuclear distance consistent with the existence of a double minimum. At the present time no transitions have been assigned in the outer minimum. However, the pulsed OODR spectra are uncharacteristically complex in this energy region.

[1] R. A. Bernheim, L. P. Gold, P. B. Kelly, T. Tipton, and D. K. Veirs, J. Chem. Phys. 76, 57 (1982).
[2] D. D. Konowalow and J. L. Fish, J. Chem. Phys. 76, 1571 (1982).

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ME6. (3:15)

ELECTRONIC TRANSITION DIPOLE MOMENT FUNCTIONS FOR NaK AND Li_2

Lyn B. Ratcliff, Daniel D. Konowalow and Walter J. Stevens

Electronic transition dipole moment functions based on full-valence configuration interaction computations (where effective core potentials are used to describe the core electrons, core-valence correlation energy, and provide for core-valence orthogonality constraints [1,2]) are calculated for alkali diatomic molecules such as NaK and Li_2. Comparison with available experimental spectra is made.

[1] W. J. Stevens, D. D. Konowalow and L. B. Ratcliff, J. Chem. Phys. 80, 1215(1984).

[2] D. D. Konowalow and J. L. Fish, Chem. Phys. 77, 435(1983).

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ME7. (3:32)

HIGH RESOLUTION FOURIER SPECTROSCOPY OF THE LASER EXCITED Cs_2 FLUORESCENCE SPECTRUM : FIVE NEW ELECTRONIC STATES

C. CREPIN, J. VERGES and C. AMIOT

The fluorescence of Cs_2 was observed inside a heat pipe oven which was operated at ~350°C. The spectra were recorded at high resolution (0.005 cm^{-1}) with a Fourier transform Interferometer.

The fluorescence excited by the Ar^+ and Kr^+ lasers was observed mainly in the 4 300 cm^{-1}, 6 500 cm^{-1}, 8 500 cm^{-1} spectral regions and also near the laser lines. The molecular constants of the pumped $E\ ^1\Sigma_u^+$ state where deduced from an analysis of the rotational relaxations and also thanks to the great number of pumped rotational levels. Molecular constants for three gerade states : (1) $^1\Pi_g$, (2) $^1\Sigma_g^+$ and (3) $^1\Sigma_g^+$ were derived from the study of the fluorescence spectra [1].

When using the ring dye laser, very high vibrational levels of the (2) $^1\Sigma_g^+$ state were observed. Triplets in the 4 200 cm^{-1} region were assigned to the fluorescence from the $D\ ^1\Sigma_u^+$ state to the 1_g component of the lowest $^3\Sigma_g^+$ state.

[1] C. AMIOT, C. CREPIN, J. VERGES. Chem. Phys. Lett. 98, 608 (1983)
    C. AMIOT, C. CREPIN, J. VERGES. Chem. Phys. Lett. (accepted)
    C. AMIOT, C. CREPIN, J. VERGES. J. Mol. Spectrosc. (submitted)

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ME8.

AN EXACT SOLUTION OF THE VIBRATIONAL MOTION OF A DISSOCIATIVE STATE. E. E. LAFLEUR AND

L. Y. CHOW CHIU

Using $U(r) = B_0 + B_1/r + B_2/r^2 + \{ \Lambda^2 - N(N+1)\}/2Mr^2$ to represent the potential
function for a diatomic dissociative state, an exact vibrational wave function is obtained.
Parameters B_0, B_1 and B_2 are to be determined from a known potential curve, Λ and N are
respectively the electronic and rotational quantum numbers and M is the reduced mass.
The solution $\psi(r) = \exp(ikr)(2kr)^S F(s+ip,2s,-2ikr)$, is shown to become a rapidly conver-
ging power series of 1 kr in the region of large (kr), and a rapidly converging power
series of kr in the region of small (kr). the two series   overlap in the intermediate
region. $k = (2ME)^{\frac{1}{2}}$, $p = B_1M/k$ and $S = \frac{1}{2} + \{ \frac{1}{4} + N(N+1) + 2MB_2 - \Lambda^2 \}^{\frac{1}{2}}$ are positive real
numbers, and E is the energy above the dissociation limit B_0. For N=0, the wave function
for the dissociative $b^3\Sigma_u^+$ state of H_2 is computed to compare with WKB wave function in
literature.[1] The calculation is extended to high N to determine the N-dependence of the
life time of the $c^3\Sigma_u$ state.

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[1]D.K. Bhattacharyya and L.-Y. Chow Chiu, J. Chem. Phys. 67, 5727 (1978).

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20059

ME9.

CALCULATION OF POTENTIAL ENERGY CURVES & FRANCK CONDON FACTORS FOR DIATOMIC MOLECULES BY USE OF THE INVERTED PERTURBATION TECHNIQUE

ERNEST A. DORKO, LYLE L. RUTGER AND JOSEPH J. POW

Potential energy curves have been calculated by the use of the Rydberg–Klein–Rees (RKR)
method and refined by use of the inverted perturbation approach (IPA) (1,2).

A program provided by C.R. Vidal was used to perform the calculations. Dunham type molecular
constants obtained by a linear least squares fit of spectroscopic data were input into the
program. The program uses the molecular constants to generate a potential energy curve for the
molecule using the RKR method. This curve is then adjusted by the IPA approach so that the
eigenvalues are consistent with the solution of the Schrodinger wave equation. In the process
of the computation, numerical eigenfunctions are obtained.

The program has been modified so that it will generate potential energy curves from the
results. A second modification to the program was made so that the numerical values for the
eigenfunctions were stored in memory. Then the Franck–Condon factors were calculated from the
eigenfunctions."

The program has been tested for two isotopes of lithium hydride and molecular iodine, and
the results have been compared to values found in the literature. The program has been used to
perform a comprehensive analysis of lead oxide. Potential energy curves have been generated for
the X, a, b, A, B, C, C', D, and E states of PbO, and Franck–Condon factors have been calculated
for transitions from each of the excited states to the ground state.

The results of these calculations are presented and discussed. A comparison is made between
the calculated Franck–Condon factors and experimentally determined relative intensities for PbO.

(1) J. Hinze and W.K. Kosman, J. Mole. Spectry., 56 93 (1975)

(2) H. Scheingraber and C.R. Vidal, J. Mole. Spectry., 65 46 (1977)

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ME10.   (4:13)

DIPOLE MOMENTS OF THE GROUND AND EXCITED VIBRATIONAL STATES OF OH AND OD

K. I. Peterson, G. T. Fraser, and W. Klemperer

OH and OD radicals were formed in a supersonically expanded discharge.[1]
The J=3/2 lambda doublet transition of OH could be observed in the $^2\pi_{3/2}$ state
for v=0, 1 and 2, but lambda doublets in the $^2\pi_{1/2}$ state were not observed.
This is consistent with the high vibrational (~3400°K) and low rotational
(~10°K) temperature measured by Droege and Engelking. The OD radical appeared
to be somewhat colder vibrationally since only the v=0 and 1 states were ob-
served, the latter being very weak. The Stark effects of the F=2→2 transition
of OH and the F=5/2→5/2 transition of OD in the J=3/2, $^2\pi_{3/2}$ state were measured
using the molecular beam electric resonance technique. The following dipole
moments were determined.

	OH	OD
v=0 (Debye)	1.65526(40)	1.65192(25)
v=1	1.66243(50)	
v=2	1.66461(70)[tentative]	

The dipole moment of the ground state of OH differs significantly from
previous results. This deviation will be discussed.

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[1] A. T. Droege and P. C. Engelking, Chem. Phys. Lett. 96, 316 (1983).

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ME11.   (4:30)

ACCURATE MULTIREFERENCE-CI CALCULATIONS OF RADIATIVE TRANSITION PROBABILITIES.
I. VIBRATIONAL TRANSITIONS WITHIN THE ELECTRONIC GROUND STATES OF OH, OH^-, OH^+, HF^+,
and HCL^+

H.-J. Werner, P. Rosmus, and E.-A. Reinsch

Electric dipole moment functions of the electronic ground states of several diatomic
molecules have been calculated using highly correlated multireference-configuration
expansions. From these functions, Einstein transition probability coefficients of
spontaneous emission and related quantities have been obtained. For the OH radical, the
dependence of the dipole moment function on the atomic basis set and on the number and the
structure of the reference configurations has been investigated extensively. Based on
these tests, the present results are believed to be more accurate than previous
theoretical and experimental data. Our transition probabilities differ significantly from
earlier theoretical data published by Mies,[1] which have often been used in the past. The
molecular ions OH^-, OH^+, HF^+, and HCl^+ are predicted to be stronger IR emitters than the
corresponding neutral molecules. The rotationless rates A_0 of spontaneous emission are
calculated to be 12.2, 137, 263, 618, and 217 sec^{-1} for OH, OH^-, OH^+, HF^+, and HCl^+,
respectively.

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[1] F.H. Mies, J. Mol. Spectr. 53, 150 (1974)

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ME\2.

ACCURATE MULTIREFERENCE-CI CALCULATIONS OF RADIATIVE TRANSITION PROBABILITIES. II. ELECTRONIC TRANSITIONS BETWEEN THE A AND X STATES OF CH, OH, HF^+, AND HCL^+

H.-J. Werner, P. Rosmus, W. Schaetzl, and W. Meyer

Electronic transition moment functions have been calculated from SCF, MCSCF, PNO-CI/CEPA, and MCSCF-CI wavefunctions. For CH and OH, the influence of the atomic basis set and of the size of the configuration expansion on the transition moments has been studied, and electron correlation is found to have a large effect on the results. SCF and compact MCSCF wavefunctions are not capable of yielding reliable transition moments, i.e, all the hydride lifetimes calculated from such wavefunctions are too small by 50-100 percent. The lifetimes obtained from MCSCF-CI or PNO-CI/CEPA wavefunctions, however, agree within 10-15 percent of reliable experimental data. For the lowest vibrational levels of the A states of CH, OH, HF^+, and HCl^+, the MCSCF-CI lifetimes are (experimental values in brackets): 531 ns (536), 590ns (690), 26.2μs (7.2), and 2.51 μs (2.58), respectively. According to these results the experimental value for HF^+ appears to be considerably too low.

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ME13.

ACCURATE MULTIREFERENCE-CI CALCULATIONS OF RADIATIVE TRANSITION PROBABILITIES. III. ELECTRONIC TRANSITIONS BETWEEN THE A AND X STATES OF CN, THE X,A, AND B STATES OF C_2^-, AND THE LOWEST FIVE TRIPLET STATES OF N_2

H.-J. Werner, P. Rosmus, J. Kalcher, E.-A. Reinsch, P.J. Hay, and D.C. Cartwright

Using highly correlated multireference-CI wave functions, electronic transition moment functions, radiative transition probabilities and lifetimes have been evaluated. The calculated lifetime for the $B^2\Sigma^+$ (v'=0) state of C_2^- amounts to 76.5ns, and is in excellent agreement with a recent experimental value of 77±8ns. For the (0,0) band origin at 4100 cm^{-1} of the $A^2\Pi \to X^2\Sigma^+$ transition, the rate is calculated to be $1.9 \cdot 10^4 \ sec^{-1}$. This value is extremely large compared to the rates of vibrational transitions within one electronic state of polar molecules. The calculated radiative lifetime of the $C^3\Pi_u$ state of N_2 is 36.9 ns, and is in close agreement with numerous measurements. For low vibrational levels of the $B^3\Pi_g$ state, however, the calculated lifetimes are up to 40 percent larger than experimental values, whereas the theoretical values for higher vibrational levels (v'=5-12) are in good agreement with recent more reliable LIF measurements. Empirical transition moment functions for the first positive system of N_2 appear to be considerably too steep, and the emirical transition moments at short distances are up to 100 percent too large. Radiative transition probabilities for the B-W and B-B' transitions in N_2, which are believed to be accurate within about 15 percent, are also predicted. The calculated radiative transition probabilities for the A-X transition in CN are in relatively good agreement with values obtained recently in an analysis of the solar spectrum, but show large discrepancies to former experimental values. The present MCSCF-CI results are also compared to previous complete active space SCF and first order CI results.

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ME14.   (5:00)

DIRECT OBSERVATION OF ALL QUASIBOUND ENERGY LEVELS AND LIFETIMES IN THE Na_2 $B^1\Pi_u$ STATE BY CW MODULATED GAIN SPECTROSCOPY

G.K. CHAWLA, H.J. VEDDER, AND R.W. FIELD

Much of the interest in the Na_2 $B^1\Pi_u$ state is because of the ~400 cm^{-1}, rotationless barrier to dissociation. It arises from the repulsive resonance interaction of the sodium atoms, one in the $3\ ^2S_{1/2}$ and one in the $3\ ^2P_{3/2}$ state, as they approach each other. This barrier supports seven or eight vibrational levels, some of which are observed to exhibit lifetime shortening from tunnelling through the barrier.

The last bound and all quasibound energy levels, normally inaccessible from thermally populated levels of the Na_2 ground state, have been populated via a triple resonance excitation scheme involving three single mode cw lasers, one of them being an optically pumped intramolecular Na_2 laser (OPL). The signal is detected by monitoring the change in this OPL output when the probe laser is tuned into resonance between the lower OPL level and a specific rotation-vibration energy level of the B-state.

The lifetimes are measured from the absorption linewidths. The observed values cover the range from ~88ps (~1.8GHz) to as short as ~8ps (~20GHz). A semi-classical treatment of the tunnelling lifetimes yields parameters which determine the long range form of the potential such as Van der Waals coefficients C_3 and C_6 and the exchange energy parameters.

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MF1.

PRESSURE BROADENING AND INTENSITY MEASUREMENTS FOR THE 2-0 BAND OF NO

A. G. MAKI AND A. S. PINE

A difference frequency laser spectrometer with a resolution of about 1 MHz has been used to study the line shapes of the 2-0 band of NO at pressures ranging from 0.5 to 500 Torr of NO and from 0 to 500 Torr of N_2. The spectra were digitally recorded and were least-squares fit to a Voigt profile with variable Gaussian and Lorentzian component widths as a function of pressure. The importance of collisional narrowing will be discussed. These measurements confirm the greater broadening of the $^2\Pi_{3/2}$ state compared to the $^2\Pi_{1/2}$ state. New values for the line intensities and the integrated band intensity will also be presented.

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MF2.

MEASUREMENTS OF PRESSURE BROADENING BY POLAR GASES

M. A. H. SMITH, G. A. HARVEY, D. J. RICHARDSON, R. E. THOMPSON, AND C. H. SUTTON

HF-broadened halfwidths have been determined for the first time in the ν_3 band of HCN near 3312 cm^{-1} and in the 1-0 band of HCl near 2886 cm^{-1}. These results were obtained from absorption spectra of cells filled with a 50-50 mixture of HF and N_2 which also contain small amounts of HCN, HCl and other gases. The spectra were recorded using a Fourier transform interferometer with nominal resolution 0.06 cm^{-1}, and the halfwidth values were obtained through a nonlinear least-squares spectral fitting procedure. HCN ν_3 lines were also analyzed in spectra of cells containing a mixture of HCl and N_2.

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MF3.

HCL FUNDAMENTAL ROVIBRATIONAL SELF-BROADENING COEFFICIENTS BETWEEN 200K AND 300K

C. CHACKERIAN, JR., D. GOORVITCH, AND L. P. GIVER

The temperature dependence of the HCL vibrational fundamental self-broadening is obtained from high resolution Fourier spectra using the direct retrieval technique[1]. The temperature dependence of the broadening is explained in terms of a simple "two component" phenomenological model.

[1] C. Chackerian, Jr. and G. Guelachvili, J. Mol. Spectrosc. 97, 316 (1983).

Address of Chackerian, Goorvitch, and Giver: Astrophysical Experiments Branch, NASA-Ames Research Center, Moffett Field, CA 94035

MF4.   (1:41)

PRESSURE BROADENED LINEWIDTHS AND ABSORPTION INTENSITIES OF THE FUNDAMENTAL AND FIRST OVERTONE BANDS OF DF

J. GELFAND, K. VERGES AND T. BEVILACQUA

We have measured the pressure broadened linewidths and absorption intensities for a number of rotation - vibration lines in the 1-0 and 2-0 bands of DF utilizing a Fourier transform infrared spectrometer. Individual linewidths and linestrengths, and the bandstrengths and Herman-Wallis factors will be presented.

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MF5.   (1:53)

NITROGEN-BROADENED LINES OF MONODEUTERATED METHANE IN THE 1.6-μm REGION

BARRY L. LUTZ

High-resolution spectra of the 1.6-μm region of CH_3D in ambient atmospheres of N_2 have been recorded with the Fourier Transform Spectrometer at Kitt Peak National Observatory (KPNO). Nitrogen pressures ranged from 100 to 500 torr. The total CH_3D abundance was 0.243 m-amagats at a partial pressure of 10 torr. All spectra were recorded at room temperature.

Reductions are being carried out using a spectral-fitting routine developed by J. Brault at KPNO which fits Voigt profiles to the spectral lines. Up to 66 consecutive absorption lines can be treated in an iterative least-squares algorithm in which each line is characterized by its position, its peak absorption coefficient, the halfwidths of the absorption coefficient, and its Gaussian and Lorentz components. Preliminary line strengths, Lorentz widths, and pressure shifts have been determined for a number of rotational fine-structure lines of the $3\nu_2$ band, and systematic dependences of the pressure width and shifts of both J and K have been found.

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MF6.   (2:00)

INTENSITY MEASUREMENTS IN THE 3μm BANDS OF $^{12}CH_4$ AND $^{12}C_2H_2$ AT LOW TEMPERATURES*

P. VARANASI*, S. CHUDAMANI*, L. P. GIVER and F. P. J. VALERO

Several spectra have been recorded between 150 and 198 K of the ν_3-fundamentals of $^{12}CH_4$ and $^{12}C_2H_2$, and of the $\nu_1 + \nu_5$ band of $^{12}C_2H_2$ with a spectral resolution of 0.06 cm^{-1}. A comparison is presented between measured line strengths and those listed in published compilations.

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Address of Giver and Valero: Astrophysical Experiments Branch, NASA Ames Research Center, Moffett Field, CA 92035.

MF7.

ABSOLUTE LINE STRENGTHS OF PHOSPHINE GAS IN THE 5 MICRON REGION

R. W. LOVEJOY, D. L. FRASCO, AND R. D. SCHAEFFER

Absolute strengths and wavenumbers of slightly over 200 vibration rotation lines of PH_3 gas have been measured at 296K in the spectral regions near 2156, 2161, 2193 and 2208cm^{-1} using a tunable diode laser spectrometer. Line strength measurements were reproducible to better than 5% on average and the uncertainty in line positions wash less than 0.002cm^{-1}. Selected PH_3 lines have been pressure broadened with H_2 gas and the results will be discussed.

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Address of Frasco: Chemistry Department, Whitman College, Walla Walla, Washington, 99362.

MF8.

THEORETICAL N_2-, O_2-, AND AIR-BROADENED HALFWIDTHS OF $^{16}O_3$ CALCULATED BY QUANTUM FOURIER TRANSFORM THEORY WITH REALISTIC COLLISION DYNAMICS

R.R.GAMACHE, R.W.DAVIES, AND L.S.ROTHMAN

We have evaluated collision broadened halfwidths of ozone with nitrogen and oxygen as the perturbing gases. Calculations using conventional Anderson theory[1] or quantum Fourier transform theory[2] are shown to be some 25 to 35% too low when compared to the experimental measurements[3,4]. We show that it is important to consider more realistic collision dynamics in the calculations. By replacing the classical path trajectories by non-linear trajectories with constant velocities chosen to give the equations of motion exact to first order in time we develop the interruption function in terms of the actual distance of closest approach determined by the intermolecular potential . This improvement to the theory results in N_2- and O_2- broadened halfwidths which are in good agreement with the experimental measurements.

Air-broadened halfwidths have been evaluated from the nitrogen and oxygen results via the formula

$$\gamma_{air} = 0.79 \ \gamma_{N_2} + \ 0.21 \ \gamma_{O_2} .$$

The results agree with the air-broadened measurements[3] to better than 5%.

1. P.W.Anderson, Phys.Rev.76, 647 (1949); 80, 511 (1950).
2. R.W.Davies, Phys.Rev.A12, 927 (1975).
3. C.Meunier, P.Marche, and A.Barbe, J.Mol.Spectrosc.95, 271 (1982).
4. J.Margolis, J.Quant.Spectrosc.Radiat.Transfer29, 539 (1983).

Address of Gamache: The Center for Atmospheric Research, University of
                     Lowell Research Foundation, 450 Aiken Street, Lowell, MA 01854.
Address of Davies: GTE/Sylvania, 40 Sylvan Road, Waltham, MA 02154.
Address of Rothman: Optical Physics Division, Air Force Geophysics Laboratory,
                     Hanscom AFB, Bedford, MA 01731.

MF9. (2:41)

DIODE LASER STUDIES OF ISOTOPIC OZONE BANDS NEAR 10 μm

V. MALATHY DEVI, B. S. WILLIAMS, M. A. H. SMITH, C. P. RINSLAND, J. M. HOELL, AND R. S. ROGOWSKI

Vibration-rotation spectra of the ν_3 fundamental band of $^{16}O_3$ and the five isotopes obtained by substitution of each ^{16}O atom by ^{18}O have been recorded using a tunable diode laser system at NASA Langley Research Center. The various isotopic mixtures have been prepared from 99.98% ^{16}O-enriched and 96.5% ^{18}O-enriched oxygen samples by electrical discharge. Spectra of nearly pure $^{16}O_3$, nearly pure $^{18}O_3$, and mixtures of these isotopes and $^{16}O^{16}O^{18}O$, $^{16}O^{18}O^{16}O$, $^{16}O^{18}O^{18}O$, and $^{18}O^{16}O^{18}O$ will be shown. Intensities and air-broadened halfwidths have been derived for selected lines.

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MF10. (3:10)

TUNABLE DIODE LASER MEASUREMENTS OF INTENSITIES AND AIR-BROADENED HALFWIDTHS OF THE ν_2 BAND OF HDO: RESULTS AND THEIR APPLICATION TO THE ANALYSIS OF STRATOSPHERIC SOLAR ABSORPTION SPECTRA

C. P. RINSLAND, A. GOLDMAN, V. MALATHY DEVI, B. FRIDOVICH, F. J. MURCRAY, D. G. MURCRAY, M. T. COFFEY, AND W. G. MANKIN

The first spectroscopic measurements of the D/H ratio in stratospheric water vapor have been derived from an analysis of stratospheric solar absorption spectra recorded near sunset with the balloon-borne 0.02-cm^{-1} resolution University of Denver and the aircraft-borne 0.06-cm^{-1} resolution NCAR interferometer systems and from laboratory spectra of HDO obtained at NOAA/NESDIS with a tunable diode laser system and a D-enriched sample of water vapor. The results have been obtained from measurements of the absorption of isolated lines of the ν_2 bands of H_2O and HDO in the atmospheric spectra. The laboratory data were analyzed to determine absolute intensities and air-broadened halfwidths for the HDO lines. Parameters are presented for the 13 HDO lines which are in the 1469 to 1514 cm^{-1} region.

The balloon-borne measurements indicate a D/H ratio, normalized to the reference value of 158 atomic parts per million of Standard Mean Ocean Water (SMOW), which increases from 0.55 near 18 km to 0.67 at 29 km. The aircraft measurements provide additional evidence for a large depletion in the D content of stratospheric water vapor. The same data sets have also been used to measure stratospheric CH_4. Within the experimental uncertainties, the changes in the H_2O, HDO, and CH_4 mixing ratios with altitude inferred from the balloon spectra are consistent with the hypothesis that these species are coupled in the stratosphere through the oxidation of CH_4.

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Address of Fridovich: NOAA/NESDIS, FOB #4, E/RA21, Washington, DC 20233.
Address of Coffey and Mankin: National Center for Atmospheric Research, Code 1302, Boulder, CO 80307.

MF11.

THE PRECISION OF THE LINE PARAMETERS RETRIEVED FROM A LORENTZ ABSORPTION LINE

N. TU AND J. H. SHAW

Contrary to our expectation,[1,2] the precision of the line parameters retrieved from simulated spectra of a single Lorentz line are not proportional to the SNR of the data over the range from 30 to 10^6. This behavior is caused by the nonlinear models which describe the data and by nonlinear correlations between the parameters. The results can be understood by considering simplified problems. The implications of these results to the design of experiments in quantitative spectroscopy are discussed. These analysis can be applied to other types of problems.

[1]E. Niple and J. H. Shaw, Appl. Spectros. 33, 569 (1979).

[2]Y. S. Chang and J. H. Shaw, Appl. Spectros. 31, 213 (1977).

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MF12.

IDENTIFICATION AND INTENSITIES OF THE "FORBIDDEN" $03^30 \leftarrow 00^00$ BAND OF $^{12}C^{16}O_2$

D. CHRIS BENNER AND C. P. RINSLAND

Lines of the $03^30 \leftarrow 00^00$ "forbidden" band of $^{12}C^{16}O_2$ have been identified in the 2000-cm^{-1} region of long-path, 0.01-cm^{-1} resolution laboratory absorption spectra recorded with the Fourier transform spectrometer in the McMath solar telescope at the National Solar Observatory. The spectral data were obtained at room temperature and with pressures less than 10 Torr of natural CO_2.

The $03^30 \leftarrow 00^00$ band has detectable intensity because of $\Delta\ell = 2$ Fermi interactions between the 03^30 upper level and the nearby $(11^10)_I$ and $(11^10)_{II}$ levels. Intensities of 8 P-branch lines (P24-P52), 9 Q-branch lines (Q24-Q42) and 1 R-branch line (R48) have been measured using a non-linear least squares spectral fitting technique. The strongest lines occur in the P branch and have intensities of 0.11 x 10^{-25} cm^{-1}/molecule-cm^{-2} at 296 K. The measured intensities have been analyzed with an F-factor expression derived for this case.[1] In terms of the total sample pressure, the band intensity is 0.194 ± 0.008 x 10^{-30} cm^{-1}/molecule-cm^{-2} at 296 K. The coefficient in the F factor is analogous to the Coriolis coefficient ξ and has been determined to be -0.0413 ± 0.0015. As expected by theory, its value is very close to that of ξ for the related $(11^10)_I \leftarrow 00^00$ band.

[1]R. A. Toth, Jet Propulsion Laboratory, private communications, 1984.

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Address of Rinsland: NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23665.

54

ANALYSIS OF CARBON DIOXIDE BANDS NEAR 2.2μm

M. Abubakar, M. L. Hoke, R. L. Hawkins, and J. H. Shaw

Three overlapping bands of CO_2 near 4640 cm^{-1} have been analysed by nonlinear, least-squares fitting procedures.[1] Two long-path spectra, one at a pressure of 177 torr and the other at 660 torr, recorded at room temperature with a Fourier transform spectrometer of 0.06 cm^{-1} spectral resolution were used. The absolute intensities, positions, rotational constants and half-widths of the lines were determined.

The measured intensities of the bands $(00°2)_I \leftarrow 00°0$ and $(01^12)_I \leftarrow (01^10)_I$ of $^{12}C^{16}O^{18}O$ are in good agreement with the estimates in the AFGL listing[2]. Improved values have been obtained for the intensity and band origin of $(31^10)_{III} \leftarrow 00°0$ of $^{12}C^{16}O_2$.

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[1] M. L. Hoke and J. H. Shaw, Appl. Opt. 21 935 (1982).

[2] L. S. Rothman and L. D. G. Young JQSRT 25, 505 (1981).

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HIGH TEMPERATURE $^{12}C^{16}O^{18}O$ AND $^{12}C^{18}O_2$ SPECTRA IN THE 2.7 μm REGION

M.P. ESPLIN AND L.S. ROTHMAN

In past symposiums we have reported line positions and molecular constants for several isotopic species of CO_2 in the 4.3 μm region. This work on high temperature CO_2 has now been extended into the 2.7 μm region.

The Air Force Geophysics Laboratory (AFGL) high resolution interferometer has been used to observe the absorption spectrum of $^{12}C^{16}O^{18}O$ and $^{12}C^{18}O_2$ in the 2.7 μm region. Spectra were taken at several pressures, and at temperatures up to 800K. Heating the CO_2 sample to high temperatures makes possible the observation of lines originating from excited rotation-vibration states.

Molecular constants which predict the position of spectral lines with an estimated accuracy of 0.0004 cm^{-1} will be presented.

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Address of Rothman: Optical Physics Division, U.S. Air Force Geophysics Laboratory, Hanscom Air Force Base, Massachusetts 01731.

MF15.

MOLECULAR PARAMETERS FOR CARBON DIOXIDE BANDS IN THE 3.73 - 4.17 um SPECTRAL REGION

V. MALATHY DEVI, D. C. BENNER, AND C. P. RINSLAND

Line positions and intensities of carbon dioxide transitions in the 2395-2680 cm^{-1} spectral interval have been determined from long-path, low-pressure absorption spectra recorded at 0.01-cm^{-1} resolution and at room temperature using the Fourier transform spectrometer in the McMath solar telescope complex at Kitt Peak National Observatory. A total of 17 bands belonging to the $^{12}C^{16}O_2$, $^{12}C^{16}O^{18}O$, $^{12}C^{16}O^{17}O$, and $^{13}C^{16}O^{18}O$ molecular species have been identified and unambiguous assignments have been made for over 1000 lines.

Absolute intensities have been derived for unblended lines of the various bands using a nonlinear least squares spectral fitting technique. For these measurements, the gas pressures ranged from 3 to 10 Torr in a 384 m absorption path. The measured intensities have been analyzed to determine vibrational band intensities and F-factor coefficients for the bands.

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MF16.

A CONSISTENT GLOBAL SOLUTION OF $^{12}C^{16}O_2$ VIBRATIONAL ENERGY LEVELS AND BAND STRENGTHS

R.B. WATTSON AND L.S. ROTHMAN

The Direct Numerical Diagonalization (DND) technique has been utilized for the study of the potential and dipole moment functions of $^{12}C^{16}O_2$. The present implementation is a three dimensional formulation, including three dimensionless normal coordinates, harmonic oscillator basis states, and a Given's diagonalization scheme. The $^{12}C^{16}O_2$ potential has been determined by a nonlinear least squares fitting procedure for matching the DND eigenvalues to experimentally derived vibrational energy levels. Inaccuracies due to lack of basis set completeness (i.e., finiteness of the Hamiltonian matrix) and due to truncation of the potential function expansion are discussed. A comparison of the final eigenstate energies with those determined by the twice-contact transformed Hamiltonian technique is also shown.

The eigenvectors resulting from the diagonalization are then used to similarity transform the matrix formed from a Taylor series expansion of the dipole moment operator. The solution of the Hamiltonian (i.e., the isolated, mechanical problem) is thus utilized to transform dipole moment derivatives into transition moments (i.e., the nonisolated, electrical problem). Inversion of this transform makes possible the calculation of dipole moment coefficients. Methods are discussed for dealing with the sign ambiguities arising from determining the transition moments as square roots of band strengths. "Hot" and difference band strengths can then be calculated from overtone and combination band strength data. The eigenvectors and calculated band strengths (especially the combination vs difference band strengths) are compared with Suzuki's[1] DND and Bordé's[2] contact transformation work. Also covered is the extension of this technique to future calculations of individual line strengths for general polyatomic molecules.

1. I. Suzuki, J. Mol. Spectrosc. 80, 12 (1980).
2. J. Bordé, J. Physique 39, 369 (1978).

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Address of Rothman: Optics Division, Air Force Geophysics Laboratory, Hanscom AFB, MA 01731

MF17.

A STUDY OF THE STRENGTHS AND WIDTHS OF LINES IN THE 10 μ N_2O BANDS

SHANXIONG SHEN, ZENG XIN GUO, I-SHAN CHENG

The line strengths, and foreign and self-broadened widths of 24 lines in 10 μ N_2O band have been determined by measuring transmittance vs. pressure using a branch selected N_2O laser.

As the absorbing N_2O is admitted to an evacuated 10 meter white multiple-pass absorption cell, the transmission at first decreases and then reaches a steady value. The constant value of extinction coefficient observed at pressures above 30 torr is in accord with the Lorentzian line shape, but instead, it is necessary to use Vigt line shape at the lower pressures.

The laser measurements indicate a knowledge about distributions of the line strengths, foreign and self-broadened width as a function of J-value, which is in agreement with the theoritical results. Also, the spectral line shift of about 0.09 $cm^{-1} atm^{-1}$ due to pressure increase was obtained.

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MF18.

THE EFFECT OF TEMPERATURE ON THE HALF-WIDTH OF THE ETHYLENE ABSORPTION AT 10 μ

SHEN SHANXIONG, CAI PEIPEI, ZHANG HANSHENG, I-SHAN CHENG

The line strength and Doppler width will vary only with temperature, whereas the half width will vary both with temperature and pressure. A stabilized 10 μ p(14) CO_2 laser line was used to measure the variation of absorption with temperature at constant density of ethylene . Measurements of almost complete extinction by the ethylene indicate that the 949.454 cm^{-1} and 949.501 cm^{-1} transitions are the frequencies which used to be considered.

The results of five seperate constant density runs were obtained. The curves were computer-calculated for value of the temperature dependent parameter differing by 0.1 and ranging from 0.5 to 1.2 . It is concluded that the temperature dependence of the linewidth is close to $T^{-0.6}$, while the value would be $T^{-0.5}$ according to the theoritical interpretation.

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MF19.

H_2O LINE SHAPE USING THE SINGLE PERTURBER APPROXIMATION

R.W. DAVIES, S.A. CLOUGH, AND S. FAHEY

In the previous paper we have discussed a time domain formulation of spectral line broadening which satisfies the fluctuation-dissipation theorem (detail balance). We present a simplified version of the theory, transformed to the frequency domain, which is equivalent to the single perturber approximation of Baranger. Calculations for H_2O self broadened line wings have been carried out using this treatment. Selected H_2O line widths have been calculated using the more complete form of the theory giving results in good agreement with Anderson theory. Some details of the calculations will be presented and emphasis will be placed on a discussion of the temperature dependence of the results.

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MF20.

A MOLECULAR LINE SHAPE FORMULATION: APPLICATION TO ATMOSPHERIC CONTINUUM

S.A. CLOUGH, R.W. DAVIES, F.X. KNEIZYS, AND R.H. TIPPING

A spectral line shape formulation will be developed in the context of the dipole autocorrelation function. The relationship of this approach with commonly used impact line shapes will be discussed as well as implications with respect to the far line wings associated with continuum absorption due to water vapor. A theory, which satisfies detail balance and which treats the isotropic part of the collisional physics exactly and the anistropic part through perturbation theory, will be outlined.

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MG1.   (1:00)

PULSED FOURIER TRANSFORM MICROWAVE SPECTROSCOPY AT 140 GHz*

W.F. Kolbe and B. Leskovar

A pulsed microwave spectrometer operating in the vicinity of 140 GHz for the detection of rotational transitions in gaseous molecules is described. The spectrometer incorporates a tunable Fabry Perot cavity and a subharmonically pumped superheterodyne receiver for the detection of the molecular emission signals. Sufficient power at 140 GHz to excite the molecules is produced by pulse modulating a high efficiency frequency doubler at an intermediate frequency of 30 MHz with the cavity tuned to one of the modulation sidebands.

The operation of the spectrometer is illustrated by the detection of emission signals from the 6(2,4)-6(1,5) transition of SO_2 gas. The generation of the electric dipole analog of NMR "spin-echo" signals by a $\frac{\pi}{2}$ - 2 pulse sequence is also described.

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MG2.   (1:17)

THE MICROWAVE SPECTRUM OF THE MONO-CHLOROMETHYL RADICAL, CH_2Cl

Y. Endo, S. Saito, and E. Hirota

We have previously reported the microwave spectrum of the mono-fluoromethyl radical, CH_2F, and have discussed its planarity in the ground vibronic state[1]. In the present study the microwave spectrum of its chlorine analogue, CH_2Cl, was observed for the first time. Molecular constants including the fine and hyperfine structure constants have been determined precisely for both the ^{35}Cl and ^{37}Cl species. Contrary to the case of CH_2F for which the equilibrium configuration seems to be slightly nonplanar, the CH_2Cl radical is planar judging from its small positive inertial defect. The CCl bond length determined was quite short and comparable to that of HCCl.

1. Y. Endo et al., J. Chem. Phys. 79, 1605 (1983).

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MG3.

THE MICROWAVE SPECTRUM OF THE VINOXY RADICAL, CH_2CHO

Y. ENDO, S. SAITO, AND E. HIROTA

Although the vinoxy radical has recently attracted much attention in chmical kinetics its spectroscopic data have been quite limited so that even its planarity has not been confirmed. The pure rotational spectrum of the vinoxy radical was observed for the first time in the mm-wave region using the reactions of either $C_2H_4 + (O_2)_{MW\ disch.}$ and $CH_3CHO + (CF_4)_{MW\ disch.}$, the latter reaction gaving 4-5 times stronger signal. The determined rotational constants result in a small inertial defect, supporting its planar structure. The spin-rotation interaction constants were found to be quite small, and are compatible with the fact that the resonance form $\overset{\bullet}{C}H_2-CH=O$, is more important than $CH_2=CH-\overset{\bullet}{O}$ in the ground electronic state, as have been predicted by ab initio calculations[1,2].

1. M. Dupuis et al., J. Chem. Phys. 76, 488 (1982).
2. E. S. Huyser et al., J. Am. Chem. Soc. 104, 2956 (1982).

Adress of Endo, Saito, and Hirota: Institute for Molecular Science, Okazaki 444, Japan.

MG4.

THE MICROWAVE SPECTRUM OF THE METHOXY RADICAL, CH_3O: HYPERFINE STRUCTURE AND JAHN-TELLER INTERACTION

Y. ENDO, S. SAITO, AND E. HIROTA

Zero field pure rotational transitions of the methoxy radical in the ^2E ground electronic state have been observed in the mm-wave region. The observation was made by a mini-computer controlled microwave spectrometer equipped with a fast flow 1 m free space absorption cell. The reaction $CH_3OH + (CF_4)_{MW\ disch.}$ was employed to generate the radical. The observed spectrum was found to consist of well resolved proton hyperfine components and also to be perturbed by the Jahn-Teller effect. A Hamiltonian dealing with the Jahn-Teller effect, the fine structure interactions (spin-orbit and spin-rotation), and the hyperfine interaction has been derived for the analysis, which well explained the observed spectra including the previously observed LMR results[1].

1. D. K. Russell and H. E. Radford, J. Chem. Phys. 72, 2750 (1980).

Address of Endo, Saito, and Hirota: Institute for Molecular Science, Okazaki 444, Japan.

THE MILLIMETER- AND SUBMILLIMETERWAVE SPECTRUM OF METHYL HYDROPEROXIDE

C.E. BLOM

Recently, the microwave spectrum of methyl hydroperoxide (CH_3OOH) has
been reported (1). The energy difference between the lowest vibrational
states, O^+ and O^-, was estimated to be around 15 cm^{-1}.
In order to determine an accurate Hamiltonian for CH_3OOH we are presently
investigating the millimeter- and submillimeterwave spectrum. Results for
interstate transitions between 100 GHz and the band-center at 448.7 GHz
will be presented.

(1) M. Tyblewski, R. Meyer and A. Bauder, presented at the 8th Colloquium
    on High Resolution Molecular Spectroscopy, Tours, 1983, paper H13.

Address of Blom: Physikalisch-Chemisches Institut, Justus Liebig Universität
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MICROWAVE AND MILLIMETER WAVE SPECTRA OF ISOTOPICALLY SUBSTITUTED DIAZIRINE
SPECIES: ROTATIONAL AND HYPERFINE STRUCTURE ANALYSIS AND MOLECULAR STRUCTURE

K. Möller, U. P. Verma, J. Vogt, M. Winnewisser and J. J. Christiansen

Diazirine is the only stable three-membered ring isomer of diazomethane. It
does not decompose in the gaseous phase, but can explode in the condensed
states. The rotational spectrum of ^{13}C- enriched diazirine and of the di-
deutero and monodeutero species have been measured in the microwave and
millimeter wave region up to 250 GHz. The a-type R- and Q-branch transitions
have been assigned for the ground vibrational state. A centrifugal distortion
analysis has been carried out for all isotopic species using the A-reduced
Watsonian. As in the case of the main isotopic species (1) the effects of
nuclear quadrupolar and spin-rotational interactions lead to a characteristic
hyperfine structure of the individual transitions which were analysed in
order to determine the appropiate quadrupolar and spin rotational constants.
The constants which will be reported reproduce the observed experimental
spectra. The spectroscopic constants obtained by a least squares fit are
currently being used in the analysis of the high resolution infrared spectra
of the various isotopic species and for a reevaluation of the molecular
structure.

(1) M. Bogey, M. Winnewisser and J. J. Christiansen, to be published.

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MG7.   (2:37)

MICROWAVE SPECTRUM OF METHOXYBORANE, CH_3OBH_2

Y. KAWASHIMA, H. TAKEO, AND C. MATSUMURA

A short-lived borone compound, CH_3OBH_2, has been identified in a reaction between B_2H_6 and CH_3OH by microwave spectroscope. A-type and b-type transitions of CH_3OBH_2 are observed showing A-E splittings due to the internal rotation of methyl group. These data yield the rotational constants of A species and the barrier to internal rotation. Spectra of ^{10}B, ^{13}C, and D_5 species have also been measured and the dipole moment of the normal species has been determined. The experimental conditions are as followed; a mixture of B_2H_6 and CH_3OH with the ratio of 1 to 1 was heated about 350°C in a quartz tube and pumped through a microwave cell continuously. All the measurements have been done with the copper wave guide cell at room temperature. The half life of this compound is about ten seconds in the cell.

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Address of Takeo and Matsumura: National Chemical Laboratory for Industry, Tsukuba, Ibaraki, 305, Japan.

MG8.   (3:00)

SPECTROSCOPY OF SMALL, FUNDAMENTAL SPECIES IN THE MILLIMETER AND SUBMILLIMETER SPECTRAL REGION

GRANT M. PLUMMER, J. K. MESSER, ERIC HERBST, FRANK C. DE LUCIA, PAUL HELMINGER, GEOFFREY A. BLAKE, AND K. V. L. N. SASTRY

This paper will give a brief summary of a number of recent spectroscopic projects that have been carried out in the Duke Microwave Laboratory. Species to be discussed will include HCO, LiH/LiD, HNO/DNO, CH_3OH, $HCOOCH_3$, HOOH, HNO_3, and CHD_2F. Theoretical approaches to internal rotation, unpaired electronic spin, and Born-Oppenheimer breakdown will be presented. Experimental techniques will also be discussed. In addition to the intrinsic spectroscopic importance of these species, they are also of importance in a number of astrophysical, atmospheric, and quantum electronic systems.

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Address of Helminger: Department of Physics, University of South Alabama, Mobile, Alabama 36688.
Address of Blake: Department of Chemistry, California Institute of Technology, Pasadena, California 91125.
Address of Sastry: Department of Physics, University of Brunswick, P.O. Box 4400, Fredericton, N. B., Canada, E3B 5A3.

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MG9.

STUDIES OF CO NEAR 4K

J. K. MESSER AND FRANK C. DE LUCIA

We have investigated the cooling of CO molecules in collisions with Helium near 4K. In these experiments, warm (300K) CO was injected into Helium gas at 4K. The CO then diffused through the background Helium and condensed on the walls of the container. Temperatures were calculated from a comparison of the linestrengths of several rotational transitions in the millimeter and submillimeter spectral region. Linewidths have been measured and preliminary pressure broadening parameters derived. This is an especially interesting regime in which to study rotational transitions because $kT \approx h\nu$.

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MG10.

APPLICATIONS OF THE AC STARK EFFECT IN THE MILLIMETER AND SUBMILLIMETER REGION

DAVID D. SKATRUD AND FRANK C. DE LUCIA

The AC Stark effect has been investigated in a series of millimeter and submillimeter wave experiments. Tunable gain sidebands have been produced on rotational transitions in the excited vibrational state of an optically pumped gas. We have also observed high order multi-photon rotational absorption with the application of an AC Stark field. These measurements are in quantitative agreement with theoretical predictions. In these experiments, it was possible to use structures that resulted in inhomogeneous Stark fields because the sideband frequencies had the attractive attribute of being equal to integer multiples of the applied frequency.

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MG11.

ROTATIONAL COMPONENT FREQUENCY MEASUREMENTS FOR THE GROUND, $v_{10}=1$, and $v_9=1$ VIBRATIONAL ENERGY LEVELS OF THE METHYL ACETHYLENE MOLECULE[1], J. M. WARE and J. A. ROBERTS

The rotational spectrum of the methyl acetylene molecule in the region of 17 to 70 gHz was studied in the ground, $v_9 = 1$, and $v_{10} = 1$ vibrational states. Frequency measurements obtained for the $v_{10} = 1$ and the ground vibrational rotational components were compared to previous measurements and to theoretical results in order to establish the reliability of the instrumentation. Measurements were then made for rotational frequencies of $J = 1 \rightarrow 2$ and $J = 3 \rightarrow 4$ components in the $v_9 = 1$ vibrational state. Our measurements on the ground and $v_{10} = 1$ vibrational states are in good agreement with the current theories. However, the $v_9 = 1$ data does not appear to fit the same model as the $v_{10} = 1$ data. These discrepancies will be discussed.

In addition some unassigned rotational transitions were measured in the same frequency range which appear to belong to doubly excited vibrational states. Possible assignments for these spectral components will be discussed.

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MG12.   (4:03)

PURE ROTATION AND ROTATION-VIBRATION SPECTRA OF OZONE

E. A. COHEN, H. M. PICKETT, J. S. MARGOLIS AND C. CHIU

A combined fit of 166 ground state rotational transitions, 96 excited state rotational transitions and 2828 vibration-rotation transitions taken at 0.005 cm^{-1} resolution has been completed for 16-16-16 O_3 for the (100) and (001) states. The fit is within experimental error and gives good reproduction of line intensities as well. The results will be discussed as will microwave measurements of the rotational spectra of the (010) and (020) states of the 16-16-16 species and the (010) states of both mono-18 species.

Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, California 91109, USA

MG13.   (4:20)

ROTATION-INVERSION SPECTRUM OF CYANAMIDE

W. G. READ, E. A. COHEN, AND H. M. PICKETT

The rotation-inversion spectrum of cyanamide was measured with the intent of accurately determining the inversion frequency, the A rotational constant, and numerous centrifugal distortion constants so that line positions can be calculated for interstellar molecular searches. A total of 146 rotational transitions between 7.0 - 500.0 GHz including 64 inversion-rotation frequencies were measured. These lines, along with previously reported transitions in cyanamide, were fit using a Watson Hamiltonian which includes an interaction between the lowest two inversion states. The inversion frequency is $1.486007(1)$ terahertz ($49.56787(3)$ cm^{-1}). The nuclear quadrupole coupling constants of the two lowest states and both components of the molecular dipole moment have been determined.

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MG14.

THE ROTATIONAL SPECTRUM OF FLUORONIUMYL (HF$^+$)

D. C. Hovde, E. Schäfer, S. E. Strahan, C. A. Ferrari, D. Ray, K. G. Lubic, and R. J. Saykally

We have recently measured the rotational spectrum of $X^2\Pi$ HF$^+$ by laser magnetic resonance; this measurement continues our study of the hydrogen halide ion series (HCl$^+$, HBr$^+$...). Λ-doubling and hyperfine structure from the halide nucleus was resolved in each case; for HF$^+$, hydrogen hyperfine structure was observed as well.

The magnetic resonance rotational transitions, augmented by combination differences from optical data, were analyzed using a Zeeman Hamiltonian in a single, weighted least squares fit. Eight molecular constants were determined. Current work is directed towards measuring the rotational spectrum of DF$^+$.

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Address of Schäfer: Zum Pfarrhag 2, 6238 Hofheim 6, West Germany.

Address of Ferrari: Instituto de Física, Universidade Estadual de Campinas, UNICAMP, 13100 Campinas, São Paulo, Brazil.

Address of Lubic: Herzberg Institute for Astrophysics, National Research Council, 100 Sussex Drive, Ottawa ON, Canada K1A OR6.

MH1.   (1:00)

Excited Vibrational States near Dissociation in Weakly Bound Triatomic Systems

J. G. Frey

The vibrational motion of a weakly bound M_3 complex is investigated using hyperspherical coordinates and an adiabatic separation of the radial and angular motions within the molecule. It is shown that the vibrational energy levels near dissociation correlate to an M atom orbiting about a rotating M_2 core. Application is made to the neon trimer assuming an approximate pairwise additive potential. Initial application of the method to the H_3^+ molecular ion will also be discussed.

Address of Frey: MMRD 70A-4418, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94709, USA. JGF would like to acknowledge the award of a NATO/SERC Post-Doctoral Fellowship.

MH2.   (1:12)

AN AB INITIO STUDY OF THE HARMONIC FORCE FIELDS AND VIBRATIONAL FREQUENCIES OF CF_4 AND SiF_4 *

L. A. Curtiss

The geometries, harmonic frequencies, and force fields of CF_4 and SiF_4 have been determined by use of ab initio molecular orbital theory with the STO-3G, 4-31G, and 6-31G* basis sets. The effect of inclusion of correlation has been considered using Møller Plesset theory to second order. Since sufficient experimental data are available for CF_4 and SiF_4 to determine the actual harmonic frequencies, these calculations provide an interesting test of the predictability of frequencies from ab initio theory. The differences between the calculated and experimentally derived harmonic frequencies for CF_4 and SiF_4 are similar to the differences found for smaller molecules for which harmonic frequencies are available. The theoretical force field is compared to force fields obtained from vibrational analyses of CF_4 and SiF_4 frequencies. Limitations of ab initio force fields for higher Z systems such as SiF_4 are discussed.

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AN ADJUSTED VALENCE FORCE FIELD (AVFF) FOR POLYATOMIC MOLECULES*

V. A. Maroni

A new type of approximate force field for the vibrational analysis of polyatomic molecules is being explored and tested in our laboratory. This force field, called the adjusted valence force field (AVFF), is a modified form of the generalized valence force field (GVFF), wherein the interactions between valence coordinates (bond-bond, bond-angle, and angle-angle) about a particular nonterminal atom are treated as a weighted fraction of the average value of the corresponding valence force constants. For example, the interaction between between a bond i and another bond j, k_{ij}, where i and j share a common nonterminal atom, is represented by $k_{ij} = f(K_i + K_j)/2$; K_i and K_j being the valence force constants for bonds i and j, respectively, and f the weighting factor (referred to as the interaction correlation factor). Similar relationships are developed for bond-angle and angle-angle interactions in terms of their valence force constants and the interaction correlation factor (ICF), with all of the connected interactions about a particular nonterminal atom being scaled by the same ICF. Although some physical basis for the AVFF concept can be seen in prior discussions of vibrational anlaysis methods, no evidence has been found of prior comprehensive applications of the concept. Tetrahedral molecules of the AB_4 type have been treated using a three-parameter AVFF which yields a fitting capability that is comparable in accuracy to a three-parameter orbital valence force field (OVFF) and is generally superior to a three-parameter Urey-Bradley force field (UBFF). An expanded version of the AVFF, incorporating a term for nonconnected interactions, has shown impressive agreement with the accurately determined potential functions derived for molecules that have well established harmonic frequencies (including those for isotopic molecules) and Coriolis constants, such as CF_4, SiF_4, and ONF. The application of the AVFF to these molecules and to several large molecules with multiple nonterminal atoms will be presented and discussed.

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THE VIBRATIONAL SPECTRUM OF FORMYL BROMIDE, HBrCO

P.D. MAKER, H. Niki, L.P. Breitenbach and C.M. Savage

Formyl bromide was prepared in-situ by the near-uv photolysis of the gases formaldehyde and bromine in 1 atm nitrogen. It had ~1.5 min half-life in conditioned cells, permitting the recording at resolution up to $1/16$ cm^{-1} of its 3-20 micron absorption spectrum by FT-IR. Apart from ν_5 (expected near 360 cm^{-1}) all fundamentals were identified for HBrCO, DBrCO, and HBr^{13}CO. Giant Fermi resonance (forbidden band intensitiy >30% of allowed band) mixed several bands: ν_2 and $2\nu_6$ in HBrCO and HBr^{13}CO; ν_3 and $2\nu_4$ in HBrCO; and ν_3 and $\nu_4+\nu_5$ in DBrCO. Typical of the formyl halides, the out-of-plane band (ν_6) was very weak and of unexpected shape. The following vibrational frequencies were determined using a simple one allowed- one forbidden-transition model for the Fermi resonances and fitting calculated rotational band contours to the observed shapes:

	ν_1 ν_{C-H}	ν_2 ν_{C-O}	ν_3 δ_H	ν_4 δ_{Br}	ν_6 $\delta_{O.P.}$
HBrCO	2912.5	1789.6[a]	1276.2[b]	646.0	894.0
DBrCO	2207.1	1748.6	969.2[c]	605.9	746.8
HBR^{13}CO	2902.7	1752.4[d]	1273.4	627.6	882.2

a) Observed at 1798.4, in Fermi resonance with $2\nu_6$ at 1774.5, intensity ratio = 0.58
b) Observed at 1271.2, in Fermi resonance with $2\nu_4$ at 1290.1, intensity ratio = 0.36
c) Observed at 975.8, in Fermi resonance with $\nu_4+\nu_5$ at 956.7, intensity ratio = 0.52
d) Observed at 1745.5, in Fermi resonance with $2\nu_6$ at 1767.5, intensity ratio = 0.45

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MH5. (2:03)

VIBRATIONAL SPECTRA OF CYCLOPROPYL CHLORIDE

C. J. Wurrey, P. M. Green and V. F. Kalasinsky

Infrared (4000-400 cm^{-1}) and Raman spectra of cyclopropyl chloride (C_3H_5Cl) have been recorded in gaseous, liquid and solid phases. In addition, a high-resolution (0.5 cm^{-1}) Fourier transform infrared spectrum of cyclopropyl chloride in the vapor phase has also been observed, and it reveals individual P and R branch rotational fine structure on B and C type gas phase vibration-rotation band contours. Based on all the available spectroscopic data such as the infrared gas phase band contours, the Raman depolarization ratios and the solid phase spectra, it has been possible to propose a complete vibrational assignment for this molecule, which is in excellent agreement with the vibrational assignment recently proposed for cyclopropyl bromide[1]. Furthermore, discrepancies in previous assignments for cyclopropyl chloride[2,3] have been resolved.

[1] C. J. Wurrey, R. J. Berry, Y. Y. Yeh, T. S. Little and V. F. Kalasinsky, J. Raman Spectrosc., 14, 87 (1983).

[2] T. Hirokawa, M. Hayashi and H. Murata, J. Sci. Hiroshima Univ. Ser. A: Phys. Chem. 37, 301 (1973).

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MH6. (2:15)

VIBRATIONAL SPECTRA AND BARRIER TO INTERNAL ROTATION OF VINYLSILANE

J. A. Smith, S. E. Rodgers, and V. F. Kalasinsky

The infrared and Raman spectra of gaseous vinylsilane have been recorded and used to clarify the vibrational assignments. Two series of sum and difference bands arising from combinations between the SiH_3 stretching vibrations and the low-frequency torsion have been observed in the infrared spectrum. From these data and the combination bands associated with the symmetric deformation the frequencies of the the V=1←0, 2←1, and 3←2 transitions have been deduced to be 132, 121, and 106 cm^{-1}. These transitions correspond to a barrier to internal rotation of 1.51 kcal/mole. Similar data were observed for the SiD_3 analog. High resolution infrared data for A-, B-, and C-type bands have also been analyzed and will be discussed.

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MH7.

VIBRATIONAL SPECTRA OF PERFLUOROCYCLOPROPENE: A POTENTIAL FUNCTION FOR THIS SUBSTANCE AND RELATED CYCLOPROPENES

NORMAN C. CRAIG, GINI F. FLEMING, AND JULIANTO PRANATA

A complete assignment of the vibrational fundamentals of perfluorocyclopropene is proposed. It is based on the Raman spectrum of the liquid, on infrared spectra under a variety of conditions, and on zero-order normal coordinate calculations. The fundamentals for this C_{2v} molecule are (in cm^{-1}): (a_1) 1940, 1367, 929, 709, 509, 245; (a_2) 616, 214; (b_1) 1331, 892, 781, (250); (b_2) 1109, 351, 251.

An overlay normal coordinate calculation for 3,3-difluorocyclopropene,[1] 1,3,3-trifluorocyclopropene,[2] and perfluorocyclopropene has yielded a vibrational potential function for these molecules. All force constants except those for CC stretching were fit to more than one molecule. The various CC stretching constants show an interesting pattern of strong influence of the position of fluorine substitution.

[1] N.C. Craig, R.A. MacPhail, and D.A. Spiegel, J. Phys. Chem. **82**, 1056 (1978).
[2] N.C. Craig, J.K. Alpern, and K.M. Parkin, Spectrochim. Acta **31A**, 1463 (1975).

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MH8.

VIBRATIONAL SPECTRA OF THE PERFLUOROCYCLOPROPENYL CATION: A POTENTIAL FUNCTION FOR THIS SUBSTANCE AND RELATED CATIONS

NORMAN C. CRAIG, GINI F. FLEMING, AND JULIANTO PRANATA

The perfluorocyclopropenyl cation, $F\triangle F$, is the product of the reaction of perfluorocyclopropene with Lewis acids, such as BF_3. From infrared spectra of the solid compounds, $C_3F_3^+BF_4^-$ and $C_3F_3^+SbF_6^-$, and from Raman spectra of $C_3F_3^+BF_4^-$ in solution in sulfur dioxide we have observed all but one of the spectroscopically active fundamentals of the $C_3F_3^+$ cation which has D_{3h} symmetry. An overlay normal coordinate calculation for the monofluorocation,[1] the difluoracation,[2] and the perfluorocation has led to a complete assignment of the fundamentals of the $C_3F_3^+$ cation. With calculated values in parentheses this assignment is (in cm^{-1}): (a_1') 2013, 751; (a_2') (800); (e') 1589, 998, 287; (a_2'') (250); (e") 640.

A discussion will be included of the effect of fluorine substitution on the CC stretching force constants.

[1] N.C. Craig, R.K.-Y. Lai, L.G. Matus, J.H. Miller, and S.L. Palfrey, J. Am. Chem. Soc. **102**, 38 (1980).
[2] N.C. Craig, R.K.-Y. Lai, K.W. Penfield, and I.W. Levin, J. Phys. Chem. **84**, 899 (1980).

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MH9.   (3:24)

MEDIUM RESOLUTION FAR INFRARED SPECTROSCOPY OF GASEOUS CYCLOPROPYL-
ISOTHIOCYANATE: ANALYSIS OF LARGE AMPLITUDE ANHARMONIC VIBRATIONS

D.J. Gerson

        In this paper preliminary data from the spectroscopic
analysis of cyclopropyl-NCS will be presented. A comparison of the
computed far infrared spectrum, as derived from several different
theoretical treatments, with the experimentally obtained spectrum will
be made.(1-3)

        The far infrared spectrum of cyclopropyl-NCS was recorded at
0.022 cm-1 resolution using an IBM Instruments IR/98 vacuum
interferometer equipped with Hg arc source, variable path gas cell,
metal mesh beamsplitter and Ge bolometer. Center of mass calculations
using the method of Cameron, et al (4) were performed on the
observed rotation-vibration lines, recorded at several sample vapor
pressures, inorder to determine their position. The reported band
positions are accurate to +/-0.001 cm-1.

        Application of the theoretical methods used in this paper to
liquid crystals at low temperatures will be discussed.

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4. D.G. Cameron, J.K. Kauppinen, D.J. Moffatt and H.H. Mantsch, Appl.
    Spectrosc.36, 245 (1982).

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MH10.   (3:36)

CONFORMATIONAL STABILITY AND BARRIERS TO INTERNAL ROTATION OF ISOPROPYL CARBOXALDEHYDE

J. R. DURIG, G. A. GUIRGIS, T. S. LITTLE, AND O. L. STIEFVATER

     The microwave spectrum of isopropyl carboxaldehyde has been investigated and for the
ground vibrational state of the more stable gauche conformer the rotational constants were
found to be A = 7494.39 ± 0.21, B = 4107.45 ± 0.01, and C = 2980.74 ± 0.01 MHz and for the high
energy trans A = 7706.75 ± 0.35, B = 3736.52 ± 0.02, and C = 2815.15 ± 0.01 MHz. The
respective dipole moment components for the trans and gauche conformers were determined to be:
$|\mu_a|$ = 2.82, $|\mu_c|$ = 0.46 and $|\mu_t|$ = 2.86D and $|\mu_a|$ = 2.43, $|\mu_b|$ = 0.79 and $|\mu_c|$ = 0.83 with
$|\mu_t^a|$ = 2.69D. From the far infrared spectrum of the gas the asymmetric torsion for the gauche
conformer was observed as a series of Q-branches starting at 90.3 cm^{-1} and from the Raman
spectrum of the gas, a "double jump" transition has been observed for the trans conformer at
110 cm^{-1}. From these data the asymmetric potential function has been calculated and the
following potential constants have been evaluated: V_1 = -181 ± 21, V_2 = -298 ± 19, V_3 = 392 ±
4, and V_6 = -7 ± 1 cm^{-1}. Additionally, variable temperature studies of the Raman spectrum of
the gas and liquid have been carried out and the enthalpy differences were determined to be 248
± 35 cm^{-1} and 440 ± 17 cm^{-1}, respectively. Evidence will be presented which indicates the two
methyl rotors are potentially coupled for the gauche conformer and the barrier to internal
rotation of the methyl tops has been calculated to be 1060 cm^{-1} (3031 cal/mol). These data, in
addition to a discussion of the vibrational assignment, will be discussed in relation to other
similar molecules.

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MH11.   3:53)

INFRARED AND RAMAN SPECTRA OF GASEOUS AND SOLID NITROSYL CHLORIDE

J. K. McDONALD, J. A. MERRITT, AND J. R. DURIG

The infrared and Raman spectra of gaseous and solid nitrosyl chloride, $ONCl$, have been recorded from 30 to 2200 cm^{-1}. In the spectrum of the gas, the fundamentals ν_2 and ν_3 for the isotopic species $ON^{37}Cl$ have been determined from the Raman spectra. Large shifts from gaseous frequencies were observed for the solid material. New force constants have been calculated and compared to previously reported constants. The pure infrared rotational spectrum of $ONCl$ has been recorded (20 to 120 cm^{-1}) and interpreted in terms of a slightly asymmetric prolate top with centrifugal distortion. Two series of seventeen and ten sharp Q-branches were observed for the ground state and first excited state, respectively. $A-\bar{B}$ and D_k have been determined for the two states in this study. The vibrational-rotational structure for two fundamentals was analyzed and excited vibrational state rotational constants have been obtained. Band centers were determined to be at 595.79 and 331.97 cm^{-1} for ν_2 and ν_3, respectively, for $ON^{35}Cl$.

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MH12.   (4:10)

INFRARED SPECTRA OF NONBENZENOID AROMATICS: ACEHEPTYLENE AND 3,5,8,10-TETRAMETHYL ACEHEPTYLENE

CHARLES H. CHO AND JONATHAN E. KENNY

Relatively little is known about the vibrational structure of polycyclic nonbenzenoid molecules. However, a number of interesting features should be observed because of the presence of aromatic and nonaromatic ring systems in the same molecule. The IR spectra of aceheptylene (one 5-membered aromatic ring and two seven-membered nonaromatic rings) and its tetramethyl derivative will be presented and discussed in light of these expectations.

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MH13.   (4:22)

LOCALIZED VERSUS DELOCALIZED VIBRATIONAL EXCITATION MECHANISMS

D. E. BRABHAM, E. W. CASTNER, A. DESOUZA, H. B. LEVENE AND D. S. PERRY

Different mechanisms for producing highly vibrationally excited molecules have varying tendencies to produce localized and delocalized excitations. Among those considered are overtone absorption and multiphoton absorption.

Specific reference is made to SF_6 and the Freons, $CFCl_3$, $CFCl_2$, and CF_3Cl, and the vibrational overtone spectra of these molecules are reported. Analysis of the spectra shows that upper states are selected according to their degree of local character. This conclusion applies even to these heavy atom systems which are strongly in the normal mode limit.

By contrast for infrared multiphoton absorption, it is necessary to maintain a near resonance condition to allow successive photon absorptions to occur. By the nature of single bond anharmonicities this requirement implies a maximally delocalized excitation.

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MH14. CANCELED

MH15.   (4:39)

Vibrational-Rotational Calculations on Formaldehyde

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Abstract

The energies of the lower lying vibrational-rotational states of formaldehyde and deutero-formaldehyde are calculated by a variational technique with use of the full Watson Hamiltonian.

First a study of different available force fields for formaldehyde was performed with the pure vibrational (J=0) Hamiltonian. The vibrational basis functions are products of one-dimensional harmonic oscillator functions, one corresponding to each of the six normal coordinates; the integrals are evaluated by Gauss-Hermite quadrature. Results for different force fields in internal valence displacement coordinates are compared with experiment. The best presently available force field for formaldehyde is one which is obtained by transforming a Taylor series in valence coordinates which has been obtained by fitting theory to experiment within the framework of second order perturbation theory; stretching displacements Δr are replaced by $\Delta r/r$ in such a way that the new force field is equal to the old one up through quartic terms in the Taylor series.

For this force field vibrational-rotational states were calculated for low J values and compared with experimental data. The rotational basis functions are symmetric top functions and the integrals are calculated analytically. The mixing of states through anharmonic effects and Coriolis coupling will be discussed.

72

72

72

SEMINAR OF INVITED PAPERS ON HYDROGEN

TA1.

(8:30)

ORIENTATIONAL PROPERTIES OF THE MOLECULES IN SOLID HYDROGEN

J. VAN KRANENDONK, Department of Physics, University of Toronto, Toronto,
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TA2.

(9:15)

ORIENTATIONAL ORDERING OF ORTHO-H_2 IN SOLID H_2*

H. MEYER

Solid hydrogen is usually a mixture of ortho-H_2 (angular momentum J=1, nuclear spin I=1, quadrupole moment eQ) with a mole fraction X, and of para-H_2 (J=0, I=0, eQ=0). The main orientational ordering mechanism of the o-H_2 is the anisotropic intermolecular electric quadrupole-quadrupole interaction [1]. The solid crystallizes in an hcp structure. For X ≥ 0.53, there is a first-order transition into a cubic phase with long-range orientational order, but for X ≤ 0.53, the structure stays hcp and ordering progresses in a continuous way. This latter regime with short-range order has been lately the subject of much interest and has been called "quadrupolar glass" by some authors.

This paper is a review of a number of experiments giving information on the process of orientational ordering for X ≤ 0.53. The experiments are nuclear magnetic resonance (line shapes, relaxation times, solid echoes) and thermodynamic properties (specific heat). An orientational order parameter σ is introduced and related with the orientational entropy S. The experimental σ-S relations of various ortho-H_2 concentrations in the "disordered" and long-range ordered state are compared with those expected for single particle models and small clusters of o-H_2 molecules. A suggested profile of the spectral density as a function of ordering is presented. *The question of whether solid H_2 is a glass is addressed.*

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*Research supported by NSF grant 81-02993.

[1] See I.F. Silvera, Rev. Mod. Phys. 52, 393 (1980) and J. Van Kranendonk, Solid Hydrogen, Plenum Press, N.Y. (1983).

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TA3.

(9:50)

THE RELATIONSHIP BETWEEN THE CALCULATED ABSORPTION COEFFICIENT FOR PURE ROTATIONAL TRANSITIONS IN SOLID H_2 AND THE PHONON DENSITY OF STATES*

JAMES R. GAINES, S. I. LEE, and K. NARAHARI RAO

The observed forbidden pure rotational transitions in solid H_2 are characterized by a sharp "zero phonon line" that is always accompanied by a broad phonon branch. The absorption coefficient for solid hydrogen has been calculated for the pure rotational transitions where the rotational quantum number increases by two or four units. For a particular assumption of the dispersion relationship, the absorption coefficient can be simply related to the single phonon density of states. The density of states obtained from the measured absorption coefficient in solid H_2 and this calculation is compared with that obtained by neutron scattering measurements.

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*Work supported in part by a grant from the National Science Foundation (DMR-8109493).

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TA4. (10:30)

MULTIPOLE MOMENTS OF H_2 AND ITS ISOTOPES

R. H. Tipping

The history of the determination of several multipole moments of H_2 and its isotopes will be reviewed. The interplay between theory and experiment will be illustrated using some recent experimental results in which new features become apparent at higher resolution or at higher densities. In particular, the importance of collision-induced effects for the determination of the dipole moment matrix elements of HD and the quadrupole moment matrix elements of H_2 will be discussed. Finally, some complications involved in determining higher moments, e.g. the hexadecapole moment of H_2, will also be considered.

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TA5. (11:05)

New Overtone Spectra of Solid Hydrogens

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ABSTRACT

Overtone spectra in solid H_2 and D_2 arise from the overlap and quadrupole induced dipole moments and therefore are exceedingly weak. At the same time these spectra are of special interest in interpretation of planetary spectra of outer giant planets, as well as for understanding the dynamics of the simplest of molecular crystals in which quantum effects play a significant role. Pulsed opto-acoustic spectroscopy of condensed phase materials - a technique that we have recently developed for the measurements of optical spectra having absorption coefficients as small as 10^{-7} cm^{-1} (from the visible to the infrared) has been successfully applied to yield the first observations of overtone vibrational spectra of solid H_2 for $\Delta v = 3$ and 4 near 8200 A and 6100 A respectively. In this review I will give the details of the experimental techniques and describe the new data in solid H_2, D_2 and HD.

TA6.   (11:40)

THE INDUCED SPECTRUM OF HYDROGEN IN THE CONDENSED PHASE AND ITS
IMPLICATIONS FOR THE STUDY OF THE SOLID STATE OF H_2

T.K. BALASUBRAMANIAN

Much of our knowledge of solid H_2 has emerged from an investigation of its Raman and induced infrared spectra[1]. Study of the induced spectrum of H_2 in the condensed state,which began in the late 50s, is still being pursued in various laboratories as a front line area. The very recent work of Patel and co-workers[2-4] devoted to the study of the spectrum in the regions of the first, second and third overtones has uncovered a wealth of information. A particularly interesting result is the evaluation of the transverse-optical and longitudinal-optical phonon densities in p H_2 from its infrared spectrum. The present paper aims at giving an upto date review of the spectroscopic work on condensed hydrogen.

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[4] Chien-Yu Kuo, Martha M.F.Vieira, R.J. Kerl and C.K.N. Patel, Phys. Rev.Lett. 50,256(1983).

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TB1.

ABSORPTION SPECTRUM OF NITROUS OXIDE IN THE REGION OF ν_1 AND $2\nu_2$

L. HENRY, T. K. McCUBBIN, J. L. TEFFO, AND A. VALENTIN

We report the absorption spectrum of natural and isotopicaly enriched samples of N_2O observed from 1080 to 1330 cm^{-1} using the Fourier Transform spectrometer at the University of Paris. Measurements were made at temperatures up to 250°C. Of special interest are the ℓ-doublets. In several bands it was possible to resolve low-J P-branch ℓ-doublets where the cc components had higher frequencies than the dd components. Resolved ℓ-doublets could be seen in both the P and R branches in one $\phi\phi$ band.

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TB2.

HIGH RESOLUTION FOURIER TRANSFORM STUDY OF THE MID-INFRARED BANDS OF CYCLOPROPANE

J. PLÍVA AND J. W. C. JOHNS

The fundamental bands of the cyclopropane molecule between 6.6 and 12.6 μm have been measured with a Bomem high resolution Fourier transform spectrometer. The most congested parts of the spectrum were deconvolved to an effective linewidth of ~0.002 cm^{-1}. The strong perpendicular bands in this region belong to the E' fundamentals ν_9 at 1438 cm^{-1}, ν_{10} at 1028 cm^{-1}, and ν_{11} at 868 cm^{-1}. All of these bands are affected by strong l-type resonances and also exhibit K-doubling of the high-J lines in the K" = 3 subbands resulting from matrix elements of the form $\langle v,\ell,J,K|h_2^+|v,\ell,J,K-3\rangle$. On the other hand, only a few perturbations by other states are noticeable in these bands. The structure of the ν_{11} band is not much affected by J_{xy} - Coriolis resonance with the ν_7 fundamental of species A_2'' which appears very weakly just 14 cm^{-1} below ν_{11}. A stronger perturbation is seen in the ν_9 band whose K = 16-17 subband exhibits an avoided crossing with the $2\nu_{14}$ state. Spectroscopic constants resulting from a least squares treatment of the Hamiltonian matrices including these interactions will be reported.

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TB3.

ANALYSIS OF THE PERPENDICULAR BANDS OF CYCLOPROPANE IN THE 3.3 μm REGION

D. W. MERDES, J. Plíva, and A. S. Pine

The C-H stretching region of the spectrum of the cyclopropane molecule between 2898 and 3157 cm^{-1} was recorded using the difference-frequency laser spectrometer system. Parts of the spectrum were deconvolved to ~1/2 of the Doppler width (~0.002 cm^{-1}). The main bands in this region are the fundamentals $\nu_6(A'')$ and $\nu_8(E')$ accompanied by a number of combination bands enhanced by resonances with the fundamentals. The upper state of the perpendicular band ν_8 occurring near 3022 cm^{-1} is in Fermi resonance with $\nu_2 + \nu_9$, which appears fairly strongly near 2934 cm^{-1}, and with $\nu_7 + \nu_9 + \nu_{14}$ located only 9 cm^{-1} above ν_8. Additional weaker perturbations of the ν_8 state have also been identified. The $\nu_2 + \nu_9$ combination is in turn very severely perturbed by several other states. A Hamiltonian matrix including the ν_8, $\nu_2 + \nu_9$, $\nu_7 + \nu_9 + \nu_{14}$, and several other perturbing states has been used for the treatment of the observed energy levels with the aid of our program system SYMTOP. The resulting "deperturbed" spectroscopic constants and the interaction constants will be reported. Highly accurate values of the ground state constants B_0, D_J^0, and D_{JK}^0 have also been obtained in the analysis.

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TB4.

ANALYSIS OF THE ν_9 AND ν_{10} BANDS OF ALLENE

J. CHAZELAS, J. PLÍVA, A. VALENTIN, AND L. HENRY

The perpendicular infrared bands of the degenerate vibrations ν_9 and ν_{10} of species E of allene with band origins near 999 and 841 cm^{-1} respectively were measured on the high resolution Fourier transform spectrometer of the Laboratoire de Spectronomie Moléculaire with an apparatus function of ~0.002 cm^{-1}. A total of 21 subbands with $K\Delta K$ ranging from -6 to +14 have been assigned in the ν_9 band and 26 subbands with $K\Delta K$ from -10 to +15 have been assigned in the ν_{10} band. In addition to the J_z - Coriolis and anharmonic interactions between the ν_9 and ν_{10} vibrations, these two bands exhibit many perturbations caused by interactions with the ν_3 and ν_4 vibrations as well as with the overtones $3\nu_{11}^1$, $3\nu_{11}^3$, with the combination $\nu_{11} + \nu_{11}$, and with other states. A Hamiltonian matrix which includes five perturbing states and their interactions with the ν_9 and ν_{10} upper states has been used for the treatment of the observed lines with the aid of the computer program system SYMTOP designed for the analysis of symmetric top bands with interacting upper states.

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TB5.

THE HIGH RESOLUTION SPECTRUM OF THE 4^1_0 BAND OF THE UNSTABLE MOLECULE HBF_2 NEAR 10.8 µm

M.C.L. GERRY, W. LEWIS-BEVAN, A.J. MERER AND N.P.C. WESTWOOD

The unstable molecule difluoroborane, HBF_2, has been prepared in good yield by the reaction of BF_3 with hot solid $NaBH_4$ in a flow system attached directly to a 20 m multipass cell. Measurements of the 4^1_0 c-type vibrational band have been made using a high resolution Bomem DA3.002 FTIR spectrometer with an apodized resolution of 0.004 cm^{-1}. It has been found that the original assignment of the K structure[1] is in error by one unit so that the value for v_0 has been increased by ~3 cm^{-1}. Detailed assignments of the fine structure have been made using rotational and centrifugal distortion constants for the ground state derived from the microwave spectrum, which has been remeasured to high values of J and K.

[1] L. Lynds and C.D. Bass, J. Chem. Phys., 43, 4357 (1965).

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TB6.

THE HIGH RESOLUTION SPECTRUM OF THE 4^1_0 BAND OF THE UNSTABLE MOLECULE H_2NBH_2 NEAR 7.5 µm

M.C.L. GERRY, W. LEWIS-BEVAN, A.J. MERER AND N.P.C. WESTWOOD

Aminoborane, H_2NBH_2, an inorganic analogue of ethylene, has only been positively observed in the gas phase by microwave spectroscopy[1] after pyrolysis of B_2H_6/NH_3 mixtures. Using an alternative route we now report that this unstable molecule can be prepared in excellent yield in the gas phase, thereby permitting all 9 of the 11 infrared active fundamentals between 800 and 4000 cm^{-1} to be observed together with several combination bands. The spectra, recorded on a Bomem DA3.002 FTIR spectrometer, exhibit a wealth of rotational structure and indicate severe perturbations within several of the bands. A detailed analysis of the observed bands is being carried out, starting with the 4^1_0 BN stretching frequency.

[1] M. Sugie, H. Takeo and C. Matsumura, Chem. Phys. Lett., 64, 573 (1979).

Address of Gerry, Lewis-Bevan, Merer and Westwood: Department of Chemistry, University of British Columbia, 2036 Main Mall, University Campus, Vancouver, British Columbia, V6T 1Y6, Canada.

TB7.

SIMULTANEOUS ANALYSIS OF THE v_2, v_3, v_5 AND v_6 BANDS OF CD_3F

L. HALONEN

The infrared spectrum of CD_3F from 800 to 1220 cm^{-1} measured with resolution of about 0.0045 cm^{-1} has been analyzed using a model which treats the four fundamentals $v_2(A_1)$, $v_3(A_1)$, $v_5(E)$ and $v_6(E)$ simultaneously. 62 parameters were refined freely in a least squares fit of microwave data and over 4200 upper state energy levels with $J \le 40$ obtained from the infrared spectrum. The root mean square deviations of the infrared and microwave data were $0.706 \cdot 10^{-3}$ cm^{-1} and $0.809 \cdot 10^{-5}$ cm^{-1} respectively. Practically all strong and medium strong, and even the great majority of the weak transitions have been assigned in the infrared spectrum. Due to strong Coriolis, α, r and higher order resonances, many normally "forbidden" infrared transitions have been observed which allows to determine the ground state constants A_0 and D_{K_0} with high accuracy. The energy levels in many of the observed submillimeter wave laser lines of CD_3F can now be identified.

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TB8.

HIGH RESOLUTION INFRARED SPECTRUM OF DNO_2 BELOW 1200 cm^{-1}

L. HALONEN

Infrared spectrum of deuterated nitrous acid, DNO_2, has been obtained below 1200 cm^{-1} with a resolution better than 0.01 cm^{-1}. Two conformers, cis and $trans$, can be seen in the spectrum. The ν_3, ν_4, ν_5 and ν_6 bands of the $trans$ form and the ν_4 band of the cis form have been analyzed rotationally. The ν_3 or ν_4 fundamentals of cis DNO_2 could not be found in the spectrum. All analyzed fundamentals are pure a type bands, except ν_6 which is a c type band, and they showed no b type structure. Only the ν_3 band of $trans$ DNO_2 showed signs of some local perturbations. All other fundamentals could be fitted well using Watson's S reduced Hamiltonian. The ground state combination difference data from the infrared spectrum and the previously published microwave data have been used to determine accurately the rotational and quartic centrifugal distortion constants of the ground state for both of the conformers.

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TB9.

DIODE LASER AND FT-IR SPECTRA OF THE ν_4,ν_6 and ν_3 BANDS OF FORMALDEHYDE

S. D. NADLER, S. J. DAUNT, D. C. REUTER AND J. W. C. JOHNS

High resolution FT-IR spectra has been recorded with a Bomem interferometer ($\Delta\nu$ = 0.004 cm^{-1}) and covers the region from 890 to 1580 cm^{-1}. Doppler limited diode laser data of selected regions have also been recorded. Line positions have been analysed including the extensive Coriolis coupling effects between the upper states. The diode laser data has been used to obtain absolute line strengths for H_2CO. The line position and line strength information is being compiled for use in domestic air pollution monitoring and astro-physical search applications.

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Address of Johns: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

TC1.

THE $b^4\Sigma^- \rightarrow a^4\Pi_i$ TRANSITION OF THE NO MOLECULE

K. P. Huber

Two sequences of the quartet system of NO[1] at 7900 Å ($\Delta v = 4$) and at 8700 Å ($\Delta v = 3$) have been rephotographed at high resolution. The spectra were obtained from a dc discharge in a supersonically expanding jet[2] of He + NO. The low rotational temperature achieved in the jet (~ 50 °K) results in a striking simplification of the previously very congested band structures, making it possible to proceed with a detailed rotational analysis.

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[1] P. A. Freedman and P. L. Radloff, J. Mol. Spectrosc. **88**, 225 (1981)

[2] A. T. Droege and P. C. Engelking, Chem. Phys. Lett. **96**, 316 (1983)

Address of K.P. Huber: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6

TC2.

HIGH RESOLUTION UV LASER SPECTROSCOPY ON THE NH FREE RADICAL

W. UBACHS, J.J. TER MEULEN AND A. DYMANUS

The hyperfine structure of NH in the excited electronic states $A^3\Pi$, $a^1\Delta$ and $c^1\Pi$ has been measured by laser induced fluorescence detection in a molecular beam experiment. The NH radicals were produced in a microwave discharge of NH_3 inside the molecular beam source. The $A^3\Pi \leftarrow X^3\Sigma$ transitions at 335 nm and $c^1\Pi \leftarrow a^1\Delta$ transitions at 325 nm were induced by cw UV radiation from a ring dye laser with intracavity frequency doubling.

The observed hyperfine splittings have been fitted to an effective hamiltonian containing the interactions between the H and N nuclear spins with the electronic spin and/or angular momentum. The values obtained for the coupling constants will be presented. In case of the $^1\Pi \leftarrow ^1\Delta$ transitions also the Λ-doublet splitting in the $^1\Pi$ state have been obtained. The fraction of metastable NH ($^1\Delta$) radicals produced in the NH_3 discharge is estimated to be of the order of 1% relative to the number of ground state NH radicals.

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80

TC3.

THE LOCATION AND PARENTAGE OF ELECTRONIC TRANSITIONS OF HETERONUCLEAR DIATOMIC MOLECULES CONTAINING TRANSITION METALS, USING EMPIRICAL METHODS

RONALD C. CARLSON AND THOMAS M. DUNN

There are now many detailed analyses of electronic systems of hetero-nuclear diatomic molecules containing transition metals but, as yet, there has been no general theoretical treatment of the number, location and nature of the systems to be expected. While there are obvious theoretical difficulties in calculating the energy levels of homonuclear diatomic molecules, this is not always true for heteronuclear, particularly when the constituent atoms have widely disparate energy levels.

It is possible to treat these molecules by a variant of Crystal Field Theory and to obtain parameters which are transferable, thereby enabling the location and identification of many electronic states to be 'predicted' with useful precision. The 'field' parameters, obtained from fitting the 'one-electron' species, range from 10 cm^{-1}, for I bound to metals of the first tran-sition series, to 575 cm^{-1} for N bound to metals of the second transition series and there are regular and predictable variations for the other halogens and non-metal 'ligands'.

The magnitudes of the 'one-electron' spin-orbit coupling constants also vary in a regular manner and, in many cases, serve as useful indicators to the atomic parentage of the molecular states. The extension to two- and three-electron systems will also be discussed.

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TC4.

LIFETIMES AND MAGNETIC MOMENTS OF PERTURBED ROTATIONAL LEVELS OF A $^1\Sigma^+$ BaO

S. D. Darrah and S. J. Silvers

Perturbed, single rotational levels of A $^1\Sigma^+$ BaO have been excited by a pulsed, tunable dye laser and their lifetimes, fluorescence quenching constants and magnetic moments have been measured. Lifetimes are lengthened and a magnetic moment of electronic origin is observed principally because of interaction and mixing with components of the b $^3\Pi$ state.

The perturbation of the v = 3 vibrational level is strongest at J = 19 where both a main and an extra line are seen. The lifetime of the J = 19 main level is 322 ± 11 nsec and that of the extra level is 672 ± 29 nsec. These compare with an unperturbed v = 3 lifetime of 279 ± 8 nsec.

The v = 2 level is most strongly perturbed at J = 28. The fluorescence quenching constant for this level is twice as large as that for unperturbed v = 2 rotational levels; its g - factor, which is caused by the perturbation, was determined by the Hanle effect to be $g_{J=28}$ = 0.95 ± 0.15 x 10^{-3}.

Measured lifetimes and moments are compared to values calculated from results of the deper-turbation analysis of Gottscho, Koffend and Field.[1]

[1] R. G. Gottscho, J. B. Koffend and R. W. Field, J. Mol. Spectrosc. 82, 310 (1980).

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TC5.   (10:33)

LIF STUDIES OF GROUP IIA DIMERS PRODUCED BY LASER VAPORIZATION OF THE METALS

V. E. Bondybey

Two electronic transitions of Be_2 are observed and analyzed[1]. The $X^1\Sigma_g^+$ ground state is characterized by a relatively shallow potential well with D_e ~900 cm^{-1}, r_e=2.465 Å, and $\Delta G_{\frac{1}{2}}$=223.4 cm^{-1}. The excited electronic states, $A^1\Pi_u$ (ν_{00}=21978.4 cm^{-1}, r_e=1.995Å, ω_e=686 cm^{-1}, $\omega_e x_e$ ~4.5 cm^{-1}), and $B^1\Sigma_u^+$ (ν_{00}=27857.8 cm^{-1}, r_e=2.16A, ω_e=504 cm^{-1}, $\omega_e x_e$ ~5 cm^{-1}) are both much more strongly bound. Several experiments designed to observe the lowest $^1\Pi_g$ state will be also discussed. Similar studies involving the Mg_2 and Ca_2 diatomics will be described. It is proposed that a spectrum observed previously[2] near 22000 cm^{-1} in matrix isolated Mg_2 and assigned as the forbidden $X^1\Sigma_g^+ \rightarrow {}^1\Pi_g$ transition is, in fact, due to the $A^1\Pi_u$ state, analogous to the corresponding state of Be_2. Analysis of Ca_2 spectrum confirms unambiguously the existence of a low lying $A^1\Sigma_u^+$ state in the red with ω_e ~120 cm^{-1}, as originally suggested by matrix experiments [3,4] and theoretical calculations[5].

[1] V. E. Bondybey, J. H. English, J. Chem. Phys. 80, 568 (1984).
[2] J. C. Miller, L. Andrews, J. Am. Chem. Soc. 100, 2966 (1978).
[3] J. C. Miller, L. Andrews, Chem. Phys. Lett. 50, 315 (1977).
[4] V. E. Bondybey, C. Albiston, J. Chem. Phys. 68, 3172 (1978).
[5] M. E. Rosenkrantz, M. Krauss, W. J. Stevens, Chem. Phys. Lett. 89, 4 (1982).

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TC6.   (10:50)

THE RED ABSORPTION SYSTEM OF THE Ca_2 MOLECULE

R. THOMAS HOFMANN AND DAVID O. HARRIS

We have observed the red absorption system of the Ca_2 molecule in a heat pipe oven. We used laser induced fluorescence and the filtered excitation method to measure eleven bands in the 610-660 nm. region. We have assigned the transition to the lowest $^1\Sigma_u^+$ excited state and the $^1\Sigma_g^+$ Van der Waal's ground state. These bands have numerous perturbations from a $^3\Pi_u$ state near its dissociation limit. The observed lines are fit to a model Hamiltonian to get molecular constants for the involved states.

We feel these measurements will settle a controversy about the assignment of the electronic levels in Ca_2. The excited state of the red system, which has been observed in matrix isolation studies, correlates in long range to $^1S + {}^1D$ atoms. The green system in Ca_2 has been studied in the gas phase and has the same ground state. Its excited state is the next highest $^1\Sigma_u^+$ state, which correlates to $^1S + {}^1P$ atoms.

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LASER SPECTROSCOPY OF NiO: ROTATIONAL ANALYSIS OF THE SYSTEM IV IN THE 5170 - 5500 Å REGION

VOJISLAV I. SRDANOV AND DAVID O. HARRIS

Laser-induced fluorescence of NiO formed by the reaction of sputtered Ni atoms from a hollow cathode source with oxygen or ozone was studied. Some of the bands belonging to the Rosen's System IV[1] were vibrationally and rotationally analyzed. A new vibrational assignment is proposed.

The rotational structure of the strongest band at 5176.5 Å resembles $^1\Pi-^1\Pi$ or $\Omega'=1$ to $\Omega''=1$ transition. Interesting features include a rotational perturbation in the excited state and extremely strong Ω-doubling in the lower state. This suggests the presence of nearly degenerate $\Omega=0$ electronic state which could be another component of a $^3\Sigma^-$ state in Hund's coupling case c. Preliminary rotational analysis of the 5176.5 Å band gives $r'_v= 1.73$ Å and $r''_v= 1.62$ Å for the equilibrium distances in the upper and lower electronic states.

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[1] B. Rosen, Nature, Lond., **156**, 570 (1945).

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POLARIZATION SPECTROSCOPY OF SrCl: THE $B^2\Sigma^+$ - $X^2\Sigma^+$ SYSTEM

W.E.ERNST AND J.O. SCHRÖDER

Strontium monochloride radicals were produced in a low pressure flame reaction of Sr and Cl_2. Using Doppler free polarization spectroscopy large parts of the (0,0), (1,1) and (2,2) bands of the $B^2\Sigma^+$ - $X^2\Sigma^+$ system were recorded. The identification of the dense spectra was simplified by applying microwave modulated polarization spectroscopy (MMPS)[1], a technique by which rotational transitions of the ground state are induced in order to label particular lines in the optical spectrum. About 500 lines were assigned. These optical data were combined with the results of separate microwave measurements of the $X^2\Sigma^+$ state in a weighted least squares fit yielding highly precise spectroscopic constants of the $B^2\Sigma^+$ state. For the vibrational analysis bandhead positions with $\Delta v=+1$ were included in the fit.

Furthermore microwave-optical polarization spectroscopy (MOPS)[2] was used to investigate the unknown hyperfine structure in the $X^2\Sigma^+$ state. Whereas the hfs could not be resolved at high rotational transitions under the usual conditions (FWHM $\simeq$ 1 MHz) the situation was different for $N=2\leftarrow 1$ and $N=1\leftarrow 0$ transitions. With the high sensitivity of MOPS hyperfine components with $\Delta J=0,+1$ and $\Delta F=0,\pm1$ could be observed.

[1] W.E. Ernst, Opt. Commun. **46**, 18 (1983).
[2] W.E. Ernst and T. Törring, Phys.Rev.A **27**, 875 (1983).

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TC9.

HIGH RESOLUTION LASER PHOTOACOUSTIC SPECTROSCOPY OF ICl

D. KUMAR, R. V. NAUMAN, S. P. MCGLYNN AND P. VENKATESWARLU

The photoacoustic spectrum of ICl in the presence of Argon/Helium has been recorded for the transition $A^3\Pi$ (1) ← $X^1\Sigma^+$ (0^+) in the region 15,500 to 17,500 cm^{-1} using a flash-lamp pumped, pulsed, tunable dye laser. The photoacoustic spectrometer incorporates a pulse-by-pulse signal correction technique which results in improved time-constant characteristics. The wavelength calibration markers are generated using the optogalvanic effect.

The vibrational analysis for both isotopes ICl^{35} and ICl^{37} has been carried out using the absorption data of Hulthen et al.[1] The high resolution spectrum has been recorded in small regions of a number of vibrational bands, namely (15,0), (16,0), (18,0), (20,0) and (21,0) using an intracavity etalon.

There is an indication that some of the vibrational-rotational levels in the $A^3\Pi$ (1) state relax faster than the others, making certain lines in the photoacoustic spectrum stronger than expected. Interactions with vibrational-rotational levels of the neighboring $A'^3\Pi$ (2) and $X^1\Sigma^+$(0^+) states are thought to be responsible for these incremented relaxation processes. The results obtained on the rotational structure and the relaxation processes will be discussed.
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[1] (a) E. Hulthen, N. Johnson, V. Pilsater, Arkiv For Fysik 14, 4754 (1958).
    (b) E. Hulthen, N. Jairlsaten and L. Koffman, Arkiv For Fysik 18, 479 (1960).

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Address of Venkateswarlu: Department of Physics, Alabama A & M University, Normal (Huntsville) AL 35762.

(8:30)

TD1.

VIBRATION-ROTATION HAMILTONIANS AND THE RENNER-TELLER EFFECT

N.C. HANDY

A variational method for the determination of vibronic energy levels of Renner-Teller triatomic molecules is introduced. The form of the hamiltonian and the expansion functions will be discussed. Applications to CH_2^+ and NH_2 will be presented, which include a full treatment of bend-stretch interactions and anharmonic effects.

The form of vibrational hamiltonians in internal coordinates is discussed.

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(9:05)

TD2.

CASSCF AND MULTI-REFERENCE CI CALCULATIONS OF INFRA-RED BANDSTRENGTHS FOR HCN

J. ALMLÖF, P. SIEGBAHN, M. LARSSON, U. JØRGENSEN AND B. GUSTAFSSON

Transmissions giving rise to combination bands in the region 5000-10000 cm^{-1} are expected to be the most important for calculations of stellar model atmospheres.

This contribution will present a detailed study of such bands for the HCN molecule. Using MCSCF and CI methods, the potential energy surface around the equilibrium geometry has been investigated. In addition to frequencies, the dipole intensities have been calculated for all transitions among a total of 150 vibrational states up to about 15000 cm^{-1}. It is found that the numerous weak transitions are as important as the few strong ones in determining the structure of stellar atmospheres.

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TD3.   (10:00)

THEORETICAL INVESTIGATION OF ALKALI DIMERS: POTENTIAL CURVES, TRANSITION MOMENTS, COUPLING
ELEMENTS, LIFETIMES, AND PERTURBATIONS

W. MEYER

Highly reliable ab initio techniques are combined with a phenomenological core polarization
concept for an efficient treatment of intershell correlation effects in all-electron SCF/valence
CI calculations. A single atomic parameter is sufficient to account quantitatively for inter-
shell correlation effects on all atomic and molecular properties investigated. For ground
states as well as a large number of excited states, the calculated spectroscopic constants agree
with available experimental data to about 100 cm^{-1} for D_e amd T_e, to 1 cm^{-1} for ω_e and to 0.02 A
for R_e. Lifetimes appear to be accurate to better than 2%. Rydberg series and perturbations by
doubly excited states are investigated for Li_2 and Na_2.

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TD4.   (10:35)

EXCITED STATES IN SMALL ORGANIC MOLECULES STUDIED BY CASSCF- AND CI-TYPE WAVE FUNCTIONS

P.-A. MALMQVIST, and B.O. ROOS

Results obtained from CASSCF and contracted CI calculations on some excited states
of butadiene and formaldehyde will be presented. Special emphasis has been put on the
development of atomic basis functions for a proper description of Rydberg states. A new
efficient method will be described which computes transition moments between CASSCF wave
functions with non-orthogonal molecular orbitals.

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TD5.   (11:10)

EXCITED STATES AND PHOTOCHEMICAL REACTIONS OF ORGANOMETALLICS : THEORETICAL INVESTIGATIONS

A. VEILLARD

The mechanism of photochemical reactions in organometallic chemistry is investigated
tnrough state correlation diagrams based on the symmetry and spin properties and CI calcula-
tions of the corresponding potential energy curves. The following reactions will be conside-
red :
     i) carbonyl elimination from $Fe(CO)_5$;
     ii) photosubstitution in the d^6 metal carbonyls ;
     iii) hydrogen elimination in $HCo(CO)_4$;
     iv) metal-metal bond cleavage in transition metal dimers.

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TD6

AB INITIO CALCULATION OF HYPERFINE COUPLING CONSTANTS FOR ATOMS AND SMALL RADICALS

W. MEYER, AND J. FLESCH

The spin-unrestricted self consistent electron pairs (USCEP) technique has been used to calculate hyperfine coupling constants for first-row and second-row atoms, first-row hydrides and their cations, and the radicals CH_3, NH_3^+, NH_2, C_2H_3 and CO^+. For the first time, consistently accurate results are obtained even for the notoriously difficult Fermi contact term, which is calculated in the coupled electron pair approximation from an energy derivative rather than as expectation value.

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TE1.

FORBIDDEN ROTATIONAL TRANSITIONS OF H_3^+

F.S. PAN AND T. OKA

While H_3^+ does not possess a permanent electric dipole moment in its equilibrium position, the centrifugal distortion[1] and the electrical and mechanical anharmonicity of the molecule[2] produce a small dipole moment in the ground state, and in degenerate excited states, respectively. We have calculated the frequencies and intensities of rotational transitions induced by these dipole moments. Because of the small moments of inertia and the large vibrational amplitude in H_3^+, the induced transitions are much stronger than those of ordinary symmetric top molecules[3]. The effect of the forbidden transitions on thermalization of H_3^+ in space and possibility of detecting such transitions in the laboratory and in space will be discussed.

---

[1] J.K.G. Watson, J. Mol. Spectrosc. 40, 536 (1971)

[2] I.M. Mills, J.K.G. Watson and W.L. Smith, Mol. Phys. 16, 319 (1969)

[3] T. Oka, F.O. Shimizu, T. Shimizu and J.K.G. Watson, Ap. J. Lett. 165, L15 (1971)

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TE2.

DIODE LASER STUDY OF THE ISOTOPES OF H_3^+

S.C. FOSTER AND A.R.W. McKELLAR

In a sense, H_3^+ is the simplest polyatomic molecule. Its spectrum was first detected by Oka[1] who observed the ν_2 fundamental band (≈ 2500 cm^{-1}) using an infrared difference frequency laser. At the same time, Shy, Farley, Lamb, and Wing[2] observed ν_2 for D_3^+ (≈ 1800 cm^{-1}) using an ion beam apparatus with Doppler tuning and CO laser excitation. Subsequently, Wing's group also detected H_2D^+ and HD_2^+ in the 1700-2000 cm^{-1} region (the lower frequency ends of the Coriolis-coupled ν_2 and ν_3 bands), but detailed assignments of the spectra have not yet proven possible. Very recently, Amano and Watson have observed and analyzed ν_1 of H_2D^+ (≈ 3000 cm^{-1}) with the difference frequency source.[3]

We are currently studying isotopic forms of H_3^+ using a diode laser spectrometer and a liquid-nitrogen-cooled multiple-traversal hollow-cathode cell.[4] The limited and unpredictable tuning ranges of diodes make them rather unsuitable for measuring the widespread and sparse bands of these light molecules. However, diodes still provide the best present means to cover the region from about 2000 to 2400 cm^{-1} between the practical limits of the CO laser and the difference frequency source, respectively. This region contains most of the ν_2 and ν_3 band structure for both H_2D^+ and HD_2^+. We have already observed all 4 isotopic forms: H_3^+, H_2D^+, HD_2^+, and D_3^+, but the total number of lines is limited (total ≈ 10 as of February, 1984). In collaboration with J.K.G. Watson, we are attempting to assign the observed lines, and the search for further transitions continues. The measurements to date, and their dependence on current, temperature, and $H_2:D_2$ mixing ratio will be discussed.

[1] T. Oka, Phys. Rev. Lett. 45, 531 (1980).

[2] J.T. Shy, J.W. Farley, W.E. Lamb, Jr., and W.H. Wing, Phys. Rev. Lett. 45, 535 (1980).

[3] T. Amano and J.K.G. Watson, this Symposium.

[4] F.C. Van den Heuvel and A. Dymanus, Chem. Phys. Lett. 92, 219 (1982).

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TE3. (1:59)

OBSERVATION OF THE ν_1 FUNDAMENTAL BAND OF H_2D^+

TAKAYOSHI AMANO AND J. K. G. WATSON

The ν_1 fundamental band of H_2D^+ was observed in absorption with a difference frequency laser spectrometer. The transition wavenumbers were fit to an effective Hamiltonian to determine the molecular constants. The band origin was determined to be 2992.486(38) cm⁻¹ which was about 7 cm⁻¹ lower than the value from ab initio calculations. The accuracy of the molecular constants obtained was not as good as that expected from the accuracy of the measured wavenumbers (0.002 cm⁻¹), presumably due to the Coriolis interaction between the ν_1 and ν_3 states.

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TE4. (2:16)

SPECTROSCOPIC PROPERTIES OF SMALL MOLECULAR IONS FROM AB INITIO CALCULATIONS

P. BOTSCHWINA, J. FLESCH, AND W. MEYER

Anharmonic potential energy surfaces have been calculated for several molecular ions (H_2O^+, HCO^+, HOC^+, $HOSi^+$, HCS^+, $HCNH^+$, NH_3^+, and SH_3^+) from highly correlated SCEP-CEPA wavefunctions. Using these potentials, vibrational states are obtained from suitable vibrational Hamiltonians by a variational method. IR intensities are computed from the anharmonic vibrational wavefunctions and ab initio dipole moment functions. HOC^+ appears to be an excellent emitter for transitions involving the ν_1 (OH stretch) mode.

An interpretation of the first bands of the photoelectron spectra of water and ammonia is made on the basis of calculated multidimensional Franck-Condon factors.

The isotropic hyperfine coupling constants of $H_2{}^{16}O^+$ and NH_3^+ are obtained to within 5 per cent of recently published matrix ESR data[1].

[1] L. B. Knight and J. Steadman, J. Chem. Phys. 77, 1750(1982); ibid, 78, 5940 (1983)

Adress: Fachbereich Chemie der Universität Kaiserslautern, D-6750 Kaiserslautern, West Germany

TE5. (2:33)

OBSERVATION OF THE ν_2 ($1^{\lessgtr}-0^+$) INVERSION MODE BAND OF H_3O^+ BY HIGH RESOLUTION SPECTROSCOPY

NATHAN N. Haese, DI JIA LIU, AND TAKESHI OKA

The ν_2 ($1^- - 0^+$) infrared absorption band of H_3O^+ has been observed by high resolution infrared diode laser spectroscopy. The spectra observed over the 830 to 1030 cm^{-1} region yield molecular constants which are in good agreement with purely theoretical predictions. Recent work on oxygen-18 isotopic substitution and on other spectral features will be reported.

[1] N.N. Haese and T. Oka, J. Chem. Phys. 80 572 (1984).

[2] P.R. Bunker, W.P. Kraemer, and V. Spirko, J. Mol. Spec. 101 180 (1983)

[3] P. Botschwina, P. Rosmus, and E.A. Reinsch, Chem. Phys. Lett. (in press).

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TE6. (2:50)

DIODE LASER OBSERVATION OF THE ν_3 BAND OF HCO^+

S.C. FOSTER, A.R.W. McKELLAR, AND T.J. SEARS

Last year the ν_1 band (C-H stretch) of HCO^+ (≈ 3100 cm^{-1}) was detected by Gudemann et al.[1] using a color center laser and a Doppler modulation scheme. Further measurements of ν_1 were made by Amano,[2] who used a difference frequency laser and discharge (concentration) modulation.

We have now observed the ν_3 band (C-O stretch, ≈ 2200 cm^{-1}) using a diode laser spectrometer with conventional source frequency modulation and 2f detection. The absorption cell was a large liquid-nitrogen-cooled multiple-traversal hollow cathode.[3] Eight lines in the R-branch, ranging from R(6) to R(17), were measured with an accuracy of 0.001 cm^{-1}. Combining these data with the previously measured[4] $\nu_3=1$, J=1+0 microwave transition, the following parameters were determined: $\nu_0=2183.9496$ cm^{-1}, $B'=44299.904$ MHz, and $D'=82.96$ kHz.

[1] C.S. Gudemann, M.H. Begemann, J. Pfaff, and R.J. Saykally, Phys. Rev. Lett. 50, 727 (1983).

[2] T. Amano, J. Chem. Phys. 79, 3595 (1983).

[3] F.C. Van den Heuvel and A. Dymanus, Chem. Phys. Lett. 92, 219 (1982).

[4] C.S. Gudemann and R.C. Woods, Paper TB8, 37th Symposium on Molecular Spectroscopy, Columbus, Ohio, June 1982.

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TE7.   (3:25)

THE OBSERVATION OF THE ν_1 (NH STRETCH) AND ν_2 (CH STRETCH) OF HCNH$^+$

R.S. ALTMAN, M.W. CROFTON, AND T. OKA

High resolution vibration-rotation spectra have been observed for both
the ν_1 (NH) and ν_2 (CH) stretching modes of the astrophysically important
molecular ion, HCNH$^+$, using a difference frequency laser spectrometer. This
first spectroscopic measurement of HCNH$^+$ shows that the structure is linear
with the following spectroscopic constants.

	ν_1 (NH Stretch)	ν_2 (CH Stretch)
ν_0 (cm^{-1})	3482.84409(105)	3187.86375(41)
B_1 (cm^{-1})	1.228633(38)	1.228494(19)
B_0 (cm^{-1})	1.236024(37)	1.236067(18)
D_1 (cm^{-1})	1.574(43) $\times$ 10^{-6}	1.610(22) $\times$ 10^{-6}
D_0 (cm^{-1})	1.596(42) $\times$ 10^{-6}	1.620(21) $\times$ 10^{-6}

The experimental results will also be discussed in light of several ex-
cellent theoretical calculations which have been made.

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TE8.   (3:42)

OBSERVATION OF THE ν_1(N-H) BAND OF DCNH$^+$ WITH A DIFFERENCE
FREQUENCY LASER

TAKAYOSHI AMANO

Very recently Altman, Crofton and Oka [1] succeeded in
observing the ν_1(N-H) and ν_2(C-H) bands of HCNH$^+$. This molecular ion
is supposed to play an important role in chemistry of interstellar
molecules. The deuterated species DCNH$^+$ is suggested to be a precursor
of DCN [2]. In this report, we will present the results of our observation
of the ν_1(N-H) band of DCNH$^+$ around 3460 cm^{-1}. DCNH$^+$ was generated
through a d.c. discharge modulated at about 21 kHz in a mixture of DCN
and H$_2$ ($p_{DCN} \sim 0.1$ Torr, $p_{H_2} \sim 0.8$ Torr). The observation was done with
an oil cooled multiple traversal cell, and the strongest line (around P(10))
was observed with S/N ~ 15 with time constant of 0.4 sec. From the least
squares analysis, the band origin and the rotational constants were
determined.

[1] private communication.
[2] W.D. Watson, Rev. Mod. Phys. <u>48</u>, 513 (1976).

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TE9.

INFRARED SPECTRA OF ^{4}HeH$^+$, ^{4}HeD$^+$, ^{3}HeH$^+$ AND ^{3}HeD$^+$

M.W. CROFTON, R.S. ALTMAN, N.N. HAESE, AND T. OKA

We have extended the earlier work[1,2] on the infrared spectrum of ^{3}HeH$^+$ by observing the hot band $v = 2 \leftarrow 1$ of HeH$^+$ and fundamental bands of isotopic species ^{3}HeH$^+$, ^{4}HeH$^+$, and ^{3}HeD$^+$. A difference frequency laser system and a diode laser have been used as tunable infrared sources and the ion velocity modulation technique was used for detection. A sealed off discharge tube was used to conserve ^{3}He. Six to fourteen vibration-rotation lines have been measured for each band. An analysis of the lines gave the following values for the band origins.

^{4}HeH$^+$	$v = 2 \leftarrow 1$	$2604.1469(18)$ cm^{-1}
	$(v = 1 \leftarrow 0$	$2910.9573(7)$ cm^{-1})
^{3}HeH$^+$	$v = 1 \leftarrow 0$	$2995.0487(9)$ cm^{-1}
^{4}HeD$^+$	$v = 1 \leftarrow 0$	$2310.4859(14)$ cm^{-1}
^{3}HeD$^+$	$v = 1 \leftarrow 0$	$2423.4262(18)$ cm^{-1}

All of the molecular constants agreed remarkably well with the results of ab initio calculations. The rotational constants of the four isotopes were used to determine the isotopically independent parameters Δ_{10}^{He}, Δ_{10}^{H}, and the U_{ij}. The observed variation of line intensities as a function of the He:H$_2$ mixing ratio is discussed in terms of simple ion-molecule reaction kinetics.

---

[1] D.E. Tolliver, G.A. Kyrala, and W.H. Wing, Phys. Rev. Lett. **43**, 1719 (1979)

[2] P. Bernath and T. Amano, Phys. Rev. Lett. **48**, 20 (1982)

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TE10.

OBSERVATION OF THE $v = 1 \leftarrow 0$ and $2 \leftarrow 1$ INFRARED BANDS OF KH BY DIODE LASER SPECTROSCOPY

Nathan N. Haese, Di Jia Liu, and Robert S. Altman

In an a.c. glow discharge through hydrogen and potassium vapor, the vibration-rotation spectra of potassium hydride has been observed throughout the 800-1100 cm region. The absorption lines are quite strong, suggesting KH densities of $\sim 10^{12-13}$ cm . So far we have systematically recorded the fundamental and first hot bands of the K-39 and K-41 isotopes, and we will report their analyses.

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TE11.   (4:28)

SUB-DOPPLER INFRARED LASER SPECTROSCOPY: VIBRATION-INDUCED eqQ IN $^{189}OsO_4$ AND DETERMINATION OF TETRAHEDRAL SPLITTING CONSTANTS IN $^{189}OsO_4$ AND $^{192}OsO_4$

F. SCAPPINI, J.M. FRYE, W.A. KREINER and T. OKA

The spectrum of a tetrahedral molecule (XY_4) with a quadrupolar nucleus at its center will not usually exhibit hyperfine structure from nuclear quadrupole coupling; this is due to the absence of an electric field gradient in such a highly symmetrical molecule. However, when the molecule is in a degenerate vibrational state, this symmetry is reduced to produce an electric field gradient at the nucleus and hence a resultant eqQ.

By means of sub-doppler infrared spectroscopy, using tunable microwave modulation side-bands on CO_2 laser lines, we have measured this vibration-induced eqQ in eighteen vibration-rotation transitions in the ν_3 band of $^{189}OsO_4$ $(I=3/2)$, and we have calculated, by least squares fit, the scalar and tensor coupling constants, χ_s^v and χ_t^v, to be -4.103(48) MHz and -3.090(59) MHz, respectively.

We have also determined the tetrahedral splitting constants in $^{189}OsO_4$ and $^{192}OsO_4$, by using a combination of infrared-radiofrequency double resonance and saturation Lamb dip spectroscopy. The ground state constant (D_t) and excited vibrational state constant (Z_{3t}) are listed below:

Transition	Z_{3t} (KHz)	D_t (Hz)
$^{189}OsO_4$ R(24)	395 ± 3	72 ± 18
$^{192}OsO_4$ P(30)	456 + 1	80 ± 26
P(37)	450 ± 2	72 ± 6

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TE12.   (4:45)

THE FLASHLAMP-PUMPED HCN GAS LASER
D. W. ROBINSON

Laser oscillation is observed at 337 μm in HCN gas excited by suprasil flashlamps. The output behavior is consistent only with a mechanism involving absorption in the HC stretching vibration ν_3 followed by collisional relaxation to the upper state $(\nu_1 + \nu_2)$ of the laser transition. In the pressure range of 5-100 mtorr gain is sufficient to overcome the low cavity losses of this long wavelength region. The same mechanism is consistent with an interesting, 400 μs modulation of the output when the HCN is diluted with CO. By virtue of the near resonance of the CN and CO stretching frequencies the inversion can be "stored" in the CO. This is manifested in the appearance of leisurely "relaxation oscillations". This qualitatively improbable picture is in good quantitative agreement with the observations.

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TE13.   (4:57)

OBSERVATION OF THE ν_1 BAND OF D_2H^+ BY DIFFERENCE FREQUENCY SPECTROSCOPY

K. G. LUBIC AND T. AMANO

          The ν_1 fundamental band of D_2H^+ has been detected using a tunable infrared difference frequency system. D_2H^+ was generated in a liquid-nitrogen cooled dc glow discharge using a 2:1 mixture of $D_2:H_2$. Amplitude discharge modulation was used to observe about 35 b-type transitions between 2640 and 2990 cm^{-1}. A least squares fit of the data gave values for the band origin and rotational constants.

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TF1.   (1:30)
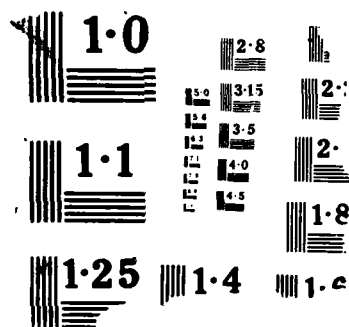
AN AB-INITIO THEORY OF VIBRATIONAL CIRCULAR DICHROISM

P.J. Stephens

A new, ab initio formalism for the calculation of vibrational rotational strengths is pre-
sented. Rotational strengths involve a product of electric and magnetic dipole transition
moments. While ab initio electric dipole transition moments are routinely calculated, magne-
tic dipole transition moments are not because the electronic contribution to the magnetic di-
pole transition moment of a vibrational transition is zero within the Born-Oppenheimer approx-
imation. This non-physical result can be overcome by using first order perturbation theory
to correct the Born-Oppenheimer approximation. The resulting expression for the magnetic di-
pole transition moment involves a sum over all excited electronic states and is not useful for
numerical calculations. We show that a contraction exists reducing the expression to one re-
quiring only ground electronic state wavefunctions. It is necessary to calculate the ground
state wave-function as a function of vibrational displacement and as a function of magnetic
field at the equilibrium geometry. An ab initio formula for a vibrational magnetic dipole
transition moment which is amenable to numerical computation is thus achieved for the first
time.

The following papers discuss the practical realization of the formalism presented.

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TF2.   (1:47)

THE VIBRATIONAL OPTICAL ACTIVITY OF TRANS-1,2-DIDEUTERIOCYCLOPROPANE

M.A. Lowe, G.A. Segal and P.J. Stephens

Calculations of the vibrational rotational strengths of trans-1,2-dideuteriocyclopropane
have been carried out using the ab initio formalism described in the previous paper. This
molecule has been used as a model system to develop and test computational aspects of the
formalism. Electronic Born-Oppenheimer wave functions along nuclear displacement coordinates
are required, as are electronic wave-functions for the molecule in the presence of a magnetic
field at the equilibrium geometry. These functions are taken to be SCF-MO functions, calcu-
lated using a modified version of the Gaussian 80 program of Pople and coworkers with a 4-31G
basis. Vibrational coordinates are obtained both from the empirical force field of Levin and
Pearce[1] and the ab initio force field of Blom and Altona[2]. The results of the ab initio
formalism are compared with those obtained from a fixed partial charge model calculation.
Sensitivity of the calculated vibrational rotational strengths to changes in force field and
to changes in equilibrium geometry will also be examined.

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[1] I.W. Levin and R.A.R. Pearce, J. Chem. Phys. 69, 2195 (1978).

[2] C.E. Blom and C. Altona, Molec. Phys. 31, 1377 (1976).

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TF3.   (2:04)

THE VIBRATIONAL OPTICAL ACTIVITY OF TRANS-1,2-DIDEUTERIOCYCLOBUTANE

M.A. Lowe, G.A. Segal and P.J. Stephens

Calculations of the vibrational rotational strengths of trans-1,2-dideuteriocyclobutane have been carried out using the ab initio formalism and computational methods described in the previous two papers, with vibrational coordinates obtained from the ab initio force field of Banhegyi, Fogarasi and Pulay[1]. The fit of the calculations to the experimental VCD spectra determined by Keiderling and co-workers will be examined. Comparison of our calculations with the predictions made by Keiderling and coworkers using the fixed partial charge and localized molecular orbital theories will also be made.

[1]G. Banhegyi, G. Fogarasi and P. Pulay, J. Molec. Struct. 82, 1 (1982).

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TF4.   (2:21)

THE VIBRATIONAL OPTICAL ACTIVITY OF PROPYLENE OXIDE

M.A. Lowe, R. Kawiecki, F. Devlin, G.A. Segal and P.J. Stephens

The vibrational absorption and CD spectrum of propylene oxide are presented and analysed. Experimental spectra have been obtained in solution at room temperature and in N_2 matrices at ∿20°K. Calculations of the VCD spectrum using various force fields and theoretical methodologies, including the new ab initio formalism, are reported and discussed. Comparison of our results with those of Polavorapu and Michalska is made.

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TF5.   (2:38)

APPLICATION OF VIBRONIC COUPLING FORMALISM TO THE DETERMINATION OF VIBRATIONAL CIRCULAR DICHROISM INTENSITIES

T. B. FREEDMAN AND L. A. NAFIE

The vibronic coupling expression for magnetic dipole interaction presented in the previous paper have been used to interpret the VCD spectra of molecules containing intramolecular rings closed by hydrogen bonding or metal ion coordination. The VCD intensities for a number of vibrational modes in these molecules cannot be adequately explained using VCD theories which employ approximate position dependent magnetic moment operators.

For alanine and cobalt complexes of alanine and ethylene diamine, the lowest energy electronic transitions involve charge transfer between the hydrogen bonded or coordinated nuclei. The vibronic coupling terms due to these electronic transitions will be shown to generate contributions to the vibrational magnetic dipole transition moment of the proper sign.

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TF6.

VIBRONIC COUPLING FORMALISM OF INFRARED ABSORPTION INTENSITY AND VIBRATIONAL CIRCULAR DICHROISM

L. A. NAFIE AND T. B. FREEDMAN

Theoretical expressions for infrared absorption due to vibrational transitions and vibrational circular dichroism will be presented in terms of vibronic coupling theory.[1] The position electric dipole representation of the interaction of radiation with matter for vibrational transitions is expressed by Herzberg-Teller vibronic coupling and reduces to the usual expression for infrared intensity as the derivative of the electric dipole moment with respect to nuclear displacement. Expressions for the momentum form of the interaction of radiation with matter and the magnetic dipole interaction are expressed by Born-Oppenheimer vibronic coupling and are formally beyond the Born-Oppenheimer approximation. It is shown, however, that these latter expressions are still adiabatic in form and describe oscillating electronic current density that is induced by the momenta, rather than the displacements, of the nuclei during vibrational motion. The significance of electronic current density for vibrational circular dichroism intensity will be discussed.

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[1] L. A. Nafie and T. B. Freedman, J. Chem. Phys. 78, 7108 (1983).

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TF7.

VIBRATIONAL CIRCULAR DICHROISM OF HYDROCHLORIDES AND SODIUM SALTS OF AMINO ACIDS

W. ZUK, J. COLBERT, AND L. NAFIE

Vibrational circular dichroism spectra will be presented for selected amino acids at pD values corresponding to the hydrochlorides and sodium salts of the compounds. Recently, L-α-amino acids at neutral pD have been shown to exhibit a strong positive VCD intensity bias associated with a methine C_α^*-H stretch.[1] This bias has been proposed to arise from an electronic ring current induced by the C_α^*-H stretching motion and supported by an intramolecular hydrogen bond between the NH_3^+ and CO_2^- groups. The data will be interpreted in terms of the strength of the VCD bias and the degree of disruption of the intramolecular hydrogen bond.

---

[1] L. A. Nafie, M. R. Obooodi, and T. B. Freedman, J. Am. Chem. Soc. 105, 7449 (1983).

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TF8.

VIBRATIONAL CIRCULAR DICHOISM of AMINO ACID DERIVATIVES

A.C. Farrell and L.A. Nafie

The vibrational circular dichroism (VCD) of various amino acid derivatives have been recorded on an FTIR spectrometer in the carbonyl stretching region. In particular, N-tert-butyloxycarbonyl-alanine has been investigated in solvents of different polarities and hydrogen-bonding characteristics (water, dimethyl-sulfoxide, and deuterochloroform). This molecule shows a strong couplet in solvents of low polarity and displays no VCD activity in an aqueous environment. The results of coupled oscillator calculations for this and other molecules will be discussed.

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TF9.

FOURIER TRANSFORM INFRARED VIBRATIONAL CIRCULAR DICHROISM OF SUGARS AND NUCLEIC ACIDS

D. M. BACK AND P. L. POLAVARAPU

We have undertaken a series of vibrational circular dichroism (VCD) measurements on sugars and nucleic acids employing a FTIR spectrometer. A correlation relating the sequential arrangement of hydroxyl groups to the sign of a VCD band near 1100 cm^{-1} is noticed from these studies. Also the VCD of 6-deoxy galactose in 1600-1300 cm^{-1} region has revealed a correlation relating the orientation of the methyl group at C_6 with respect to that of methine group at C_1. These new results and their useful implications will be discussed.

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TG1.   (1:30)

LIFETIMES OF SOME LOW-LYING EXCITED ELECTRONIC STATES OF Fe, Co AND Ni ATOMS IN SOLID INERT GAS
MATRICES

THOMAS A. CELLUCCI AND EUGENE R. NIXON

Fluorescence decay profiles were used to measure the lifetimes of several low-lying electronic states of Fe, Co and Ni atoms in solid argon and krypton. For those states for which decay is primarily by "forbidden" radiative processes, the lifetimes range from 200–1200 μsec. Some states for which non-radiative relaxation appears to dominate the lifetimes are less than 10 nsec. Results will be discussed in terms of electronic configurations.

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TG2.   (1:42)

LASER-INDUCED FLUORESCENCE STUDY OF LOW-LYING ELECTRONIC STATES OF Ni ATOMS IN SOLID INERT GAS
MATRICES

THOMAS A. CELLUCCI AND EUGENE R. NIXON

Laser-induced fluorescence studies of low-lying energy states of Ni atoms isolated in Ne, Ar and Kr matrices show that the atoms in Ne matrices are "gas-like" in nature, with a $^3F_4 (3d^8 4s^2)$ ground state and levels only slightly perturbed by the matrix environment. The Ar and Kr matrices contain not only these "gas-like" atoms but also Ni atoms in a second kind of environment. The ground state of these atoms is $^3D_3 (3d^9 4s^1)$, which we estimate lies about 200 cm^{-1} below $^3F_4$.

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TG3. (1:59)

COMPARISON OF THE GROUND-STATE VIBRATIONAL FUNDAMENTALS OF DIATOMIC MOLECULES IN THE GAS PHASE
AND IN INERT SOLID MATRICES

MARILYN E. JACOX

    Despite the voluminous literature on the spectra of diatomic molecules, there are many
gaps in our knowledge of their ground-state vibrational frequencies. For many important dia-
tomic molecules, only values obtained in matrix isolation experiments are available. In order
to assess the likely extent of deviation of the ground-state vibrational fundamentals of dia-
tomic molecules observed in rare-gas and nitrogen matrices from the gas-phase values, a sys-
tematic comparison has been made between gas-phase and matrix frequencies. The dependence of
matrix shifts on the matrix material, type of chemical bond, and position of the elements in
the Periodic Table will be considered for the approximately 225 pairs of observations which
have been reported.

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TG4. (2:16)

THE INFRARED SPECTRA OF INTERMEDIATES IN THE REACTION OF F ATOMS WITH ACETONITRILE TRAPPED IN
SOLID ARGON

MARILYN E. JACOX

    Although HF chemiluminescence has been reported in gas-phase studies of the $F + CH_3CN$
reaction, the spectrum of the CH_2CN free radical has not been identified, and the extent to
which competing F-atom addition reactions occur has not been assessed. When the products of
this reaction are trapped in solid argon at 14 K, a rich infrared spectrum is obtained, with
evidence for the occurrence of both H-atom abstraction and F-atom addition. The results of
detailed concentration dependence and isotopic substitution studies will be presented, and
vibrational assignments for such products as CH_2CN and CH_3CFCN will be discussed.

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TG5. (2:33)

SPECTROSCOPIC INVESTIGATION OF HSNO IN A LOW TEMPERATURE MATRIX. UV, VIS, AND IR INDUCED
ISOMERIZATIONS

R.P. Müller, M. Nonella, and J.Robert Huber

    An infrared spectroscopic investigation has been performed on the trans and cis isomers
of thionitrous acid (HSNO) and their D- and ^{15}NO-isotopic modifications in argon matrices at
12 K. The substances were prepared photolytically from thionylimid (HNSO) isotopes in the
matrix. With UV (250 nm), VIS (585 nm), and IR irradiation the cis → trans or the trans → cis
isomerization of HSNO was induced, allowing an unequivocal distinction between the closely
resembling IR spectra of the trans and cis isomers. Complete set of fundamental frequencies
of both rotamers were obtained and assigned by normal coordinate analysis using the transfer-
able valence force field (TVFF) approach. Parallel to this analysis ab-initio calculations
on the SCF- and CI-levels were performed to predict energy, geometry, and barrier of internal
rotation for the two HSNO rotamers. These results and those of a parallel study on methyl-
thionitrite (CH_3SNO) are discussed and compared to the behavior of the nitrite molecules
HONO and CH_3ONO.

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(2:50)

TG6.

FTIR SPECTRA OF THE HYDROGEN-BONDED COMPLEX WITH PHOSPHINE AND HF IN SOLID ARGON

R.T. ARLINGHAUS AND L. ANDREWS

Codeposition of Ar/PH_3 and Ar/HF samples at 12K produced new absorptions at 3628, 843 and 477 cm^{-1}. Similar experiments with DF gave product bands at 2673, 678 and 366 cm^{-1}. These bands are assigned to the ν_s (H-F stretching), $2\nu_\ell$ and ν_ℓ (H-F librational) modes, respectively, in the H_3P--HF hydrogen-bonded complex based on HF/DF ratios of 1.357, 1.243 and 1.303. The observation of a single sharp ν_ℓ mode indicates that the complex has the C_{3v} structure in solid argon as deduced for the gaseous species.[1]

A quadratic-quartic potential function for the librational coordinate $\Delta(r\theta)$ has been calculated from the $2\nu_\ell$ and ν_ℓ observations. The classical turning point for the $v = 0$ level is 16°, in good agreement with the 20° value deduced from coupling constants[1] for this angle averaged over zero-point motion.

Comparisons will be made with the H_3N--HF complex reported earlier[2] and new data for the H_3As--HF and H_3Sb--HF species.

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[1] A.C. Legon and L.C. Willoughby, Chem. Phys. **74**, 127 (1983).

[2] G.L. Johnson and L. Andrews, J. Am. Chem. Soc. **104**, 3043 (1982) and unpublished results.

Address of Authors: Chemistry Department, University of Virginia, Charlottesville, VA 22901.

(3:30)

TG7.

INFRARED SPECTRA OF DEUTERATED ISOTOPOMERS ISOLATED IN H_2O CLATHRATES

H. H. Richardson, P. J. Wooldridge and J. P. Devlin

A reliable procedure for the preparation of clathrate hydrates as low-temperature thin films was recently described[1]. Amorphous films, prepared with the proper host-guest molar ratios by codepostion at T<80K, crystallize to the hydrate at temperatures in the 110-125 K range. This procedure permits the incorporation of intact deuterated isotopomers either as part of the host lattice, i.e. D_2O, or as caged guest molecules, eg. D_2S in an H_2O latttice.

This ability to trap intact isotopomers opens up two areas of investigation: 1) the dynamics of molecules isotopically decoupled in the clathrate stucture (host or guest) and 2) the kinetics of proton exchange as evidenced by the conversion of intact isotopomers to isotopically mixed molecular species. In particular, the vibrational spectrum of D_2O isolated in the H_2O ethylene oxide clathrate has been measured for comparison with the corresponding crystalline ice I_c data and the spectra of both H_2S and D_2S, as guests in the two sizes of type I clathrate cages, have been obtained.

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1. J. E. Bertie and J. P. Devlin, J. Chem. Phys. **78**, 6340, 1983.

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078.

TG8. (3:47)

MATRIX SPECTRA OF ION-PAIR SOLVATES, $S_n \cdot Li^+NO_3^-$

G. Ritzhaupt, K. Consani and J. P. Devlin

The vibrational spectra of bare ion pairs, such as $Li^+NO_3^-$, accurately reflect the magnitude of the cation distortion of the anion through the splitting of otherwise degenerate modes. These large splittings (262 cm^{-1} for $Li^+NO_3^-$ in an argon matrix) also provide a useful probe of the effect of cation solvation on the ion pairs since complete solvation, as occurs in liquid solutions of non-dissociating solvents, results in near-collapse of the splitting.

The effect of individual solvation steps on the ion pairs can be studied by the measurement of infrared spectra for species such as $S_1 \cdot LiNO_3$, $S_2 \cdot LiNO_3$ etc. prepared in inert gas matrices containing an appropriate fraction of the solvent, S. High quality FT-IR spectra allow the evaluation of reliable cation solvation numbers, an insight to the nature of the anion-solvent interaction, and an analysis of the interplay between cation-solvent bonding and steric forces within the cation solvation shell.

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TG9. (4:04)

INFRARED MATRIX ISOLATION SPECTROSCOPIC STUDIES OF THE COMPLEXES OF CYCLOPROPANE AND METHYL-SUBSTITUTED CYCLOPROPANES WITH THE HYDROGEN HALIDES

CANDACE E. TRUSCOTT AND BRUCE S. AULT

Infrared matrix isolation spectroscopy has been used to isolate and characterize the 1:1 complexes formed by the hydrogen halides and cyanide with cyclopropane and a variety of methyl-substituted cyclopropanes. Perturbed modes of the cyclopropane ring were observed for each of the complexes studied, and a reduction in symmetry was noted for the cyclopropane complexes. In addition, the H-X stretching mode in the complex appeared shifted to lower energies, by up to 200 cm^{-1}, indicating the formation of a hydrogen bond. The magnitude of the shift and the degree of perturbation of the ring correlated with the strength of interaction and dipole moment of the acid. The spectral results are in agreement with the structure of the $HX \cdot c\text{-}C_3H_6$ complexes as determined by rotational spectroscopy in supersonic jets. The site of coordination in the methyl-substituted cyclopropane is not known, and these studies may shed additional light on the mechanism of acid-catalyzed ring openings of substituted cyclopropanes.

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TG10. (4:21)

INFRARED MATRIX ISOLATION STUDY OF THE 1:1 COMPLEXES BETWEEN THIONYL FLUORIDE AND SULFUR TETRAFLUORIDE AND SUBSTITUTED AMINES

CRAIG S. SASS AND BRUCE S. AULT

The matrix isolation technique has been applied to the investigation of the sulfur-nitrogen coordinate bond in 14 K nitrogen matrices. The codeposition of ammonia and sulfur tetrafluoride gave rise to a 1:1 complex characterized by four sulfur-fluorine stretching modes of the SF_4 subunit at 675, 830, 881 and 905 cm^{-1}. In addition, the symmetric deformation mode of the NH_3 subunit was identified at 1242 cm^{-1}. The large shift of this mode from the parent position of 972 cm^{-1} indicates that the complex is relatively strongly bound. 1:1 complexes were also observed between ammonia and thionyl fluoride (SOF_2) and sulfuryl fluoride (SO_2F_2); these complexes, however, were bound much less strongly. By comparison, no complex was observed when NH_3 was codeposited with $SOCl_2$. In addition, no complexes of trimethyl amine could be isolated, and only one complex of monomethylamine, with SOF_2. The relative shifts of the S-F stretching modes of the SOF_2 subunit in this complex relative to the NH_3 complex indicate that the $SF_4 \cdot CH_3NH_2$ complex is more strongly bound. However, the low yield suggests a significant barrier to reaction.

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A. C. WAHL MEMORIAL SESSION

TH1.   (1:30)

GROWTH TO MATURITY OF THE MCSCF MODEL   (INVITED PAPER)

C. C. J. ROOTHAAN, Departments of Chemistry and Physics, University of Chicago, Chicago, Illinois, 60637.

TH2.   (1:52)

ELECTRONIC STRUCTURE OF THE HELIUM MOLECULAR ANION, HE_2^-

H. H. Michels*

The recently discovered,[1] long-lived metastable He_2^- ion is examined using configuration-interaction wavefunctions constructed from an extended STO basis. We find that the $^4\Pi_g$ state of He_2^- is bound relative to the $a^3\Sigma_u^+$ state of He_2 for all internuclear separations greater than 0.8Å. The calculated electron affinity is 0.233 eV compared to .077 eV for the He^- [$^4P°$] atomic ion. There are no other symmetries of He_2^- that exhibit overall stability relative to He_2 [$a^3\Sigma_u^+$]. We conclude that this anion decays through the long-lived 5/2g component with $\tau \sim 350$ µsec and the much shorter-lived 3/2g, 1/2g components with $\tau \sim 10$ µsec.

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[1] Y. K. Bae, M. J. Coggiola and J. R. Peterson, Phys. Rev. Lett., in press.

Address: United Technologies Research Center, East Hartford, Connecticut, 06108.

TH3.   (2:04)

A VARIATION METHOD FOR THE CALCULATION OF DYNAMIC POLARIZABILITIES AND TWO-PHOTON TRANSITION MOMENTS. THE DRESSED MOLECULE APPROACH

Winifred M. Huo

It is well recognized that the solution of the time-dependent Schrödinger equation for the molecule + radiation field system is oscillatory. The three methods frequently used for the calculation of dynamic polarizabilities: perturbation, variation-perturbation, and time-dependent Hartree-Fock or Multi-Configuration Hartree-Fock, are all based on the oscillatory nature of the wavefunction. However, Cohen-Tannoudji and his coworkers[1] showed that a large number of experimental data associated with the behavior of molecules in a strong radiation field can be explained using the dressed molecule representation where the coupling Hamiltonian is diagonalized in a basis of non-interacting photon + molecule states. To understand the relationship between the oscillatory function and the dressed state wavefunction, the solution of the time-dependent Schrödinger equation of the molecule + radiation field system is analyzed with the radiation field quantized. It is found that the oscillatory wavefunction is the proper solution if the radiation field is turned on at t=0 and the dressed state is a stationary solution satisfying the boundary condition only if the field is present at t=- ∞. In general, the oscillatory wavefunction can be generated using a complete set of dressed states. However, in the presence of a nonresonant radiation field, the molecule is in one single dressed state almost all the time. In that case, the dynamic polarizability can be deduced from the level shift of the dressed state and the two-photon transition moment can be expressed as a one-photon transition moment between the dressed state and the final state of the two-photon transition. Because of its stationary character, the dressed state wavefunction is amenable to approximate calculations. A CI method is developed for such calculations. The CI matrix is simple in form, and can be readily constructed using existing computer codes. Numerical examples using this method will be given.

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[1] C. Cohen-Tannoudji and S. Reynaud. J. Phys. B10, 345 (1977).

Address of Huo: Radiation Laboratory, University of Notre Name, IN 46556 Mailing Address: NASA Ames Research Center, Mail Stop 230-3 Moffett Field, CA 94035

TH4. (2:21)

ELECTRONIC STRUCTURE OF FeO, RuO, FeH, AND RuH

M. KRAUSS AND W. J. STEVENS

The electronic structure of FeO and RuO was calculated in a multi-configuration self-consistent-field (MC-SCF) where three sigma, two pi, and one delta orbitals were considered as open valence orbitals and all configurations that arise from this space were optimized (complete active space (CAS)). Relativistic effective potentials (REP) were used to both simplify the integral and SCF calculations and to make the calculation of the spin-orbit interaction tractable. The calculated ground state spectroscopic constants for FeO are not in good agreement with experimental values but the values for the ground state of RuO are reasonable. The values for the $^5\pi$ and $^5\phi$ excited states of FeO are also in accord with experiment, and the calculated spin-orbit constants for these states support the assignment. The observation of different levels of accuracy for different states can be rationalized in terms of differential correlation effects.

The CAS-MC-SCF results for FeH and RuH were obtained with an open valence space of four sigma, two pi, and one delta. For FeH the $^6\Delta$ is found lowest in energy at this level of calculation, which is not in accord with the experimental assignment. The $^4\Delta$ is a close-lying excited state for FeH, but is lower in energy than the $^6\Delta$ for RuH. However, as would be evident from the atomic level differences from Fe and Ru, the ground state of RuH is calculated to be a $^4\Sigma$ state.

The electronic structure of the ground and low-lying excited states will be discussed as well as the effects of correlation on the structure. The electronic structure of the ground state of the negative ions as determined at this level of approximation will be noted.

Address of Krauss and Stevens: Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C. 20234.

TH5. (2:38)

FIELD-THEORETIC METHODS FOR SEPARATED-PAIR BCS FUNCTIONS
W. B. ENGLAND, D. M. SILVER, AND E. O. STEINBORN

The motivation for this work arose in large part from the belief that the intuitive ideas of A. C. Wahl,[1] originally expressed as ODC wave functions shortly after his accurate calculations of the Hartree-Fock wave function of F_2,[2] could be combined with the methods of superconductivity theory.

We have now derived a formalism which applies to BCS functions which have the proper symmetries of the problem and whose particle fluctuations are rigorously compensated. This is accomplished by a generalization of Lipkin's model-Hamiltonian method[3] for wave packets that gives as zeroth-order a separated-pair theory. Since our zeroth-order function is a BCS function, we are able to define the contributions of higher-orders rigorously using essentially ordinary Feynman diagrams and rules for their evaluation. After carrying out systematic orbital and operator transformations,[4] the perturbation theory becomes even simpler than its forebear proposed by Nambu.[5] This transpires because we are able to derive charge distributions that accommodate the new 1-particle states and their fractional occupancies simultaneously, and because the 2 X 2 propagator matrices become essentially idempotent.

At present, we have explicit expressions for all diagrams through third order which arise from the 2-body Lipkin Hamiltonian. In the (unlikely) event that we will have calculations completed for F_2 before this symposium, these will be described.

[1] G. Das and A. C. Wahl, J. Chem. Phys. 44, 87(1966)
[2] A. C. Wahl, J. Chem. Phys. 41, 2600(1964)
[3] H. J. Lipkin, Ann. Phys. (NY) 9, 272(1960)
[4] J. G. Valatin, Phys. Rev. 122, 1012(1960)
[5] Y. Nambu, Phys. Rev. 117, 648(1960)

Address of England: Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201
Address of Silver: Johns Hopkins University, Applied Physics Laboratory, Laurel, Maryland 20707
Address of Steinborn: Institut für Physikalische und Theoretische Chemie, Universität Regensburg, D-8400 Regensburg, West Germany

TH6.   (2:55)

Ab-initio COUPLING COEFFICIENTS BETWEEN THE LOWEST IONIC AND COVALENT STATES OF KBr_2

E.M. GOLDFIELD, E.A. GISLASON and N.H. SABELLI

We will present results of an ab-initio MCSCF/CI study of the curve crossing region for linear KBr_2. The calculations were performed with effective core potentials[1] for both Br and K^2 and a valence double zeta plus polarization basis set. A single set of MCSCF orbitals was used to perform the CI; the configuration list included up to quadruple excitations from a multireference set.

The distance between K and the center of mass of Br_2 was fixed at 15 a.u., which places the system in the region where a vibrational barrier has been postulated. The barrier has been found in a DIM calculation[3].

We have also calculated coupling matrix elements between the diabatic ionic and covalent states. We shall report energies and matrix elements and compare them with estimates obtained from semiempirical models[3,4].

1.- P.J. Hay, W.R. Wadt and L.R. Kahn, J. Chem. Phys. v68, 3059 (1978)
2.- W.R. Wadt, private communication
3.- E.M. Goldfield, E.A. Gislason and N.H. Sabelli, submitted for publication
4.- R. Grice and D.R. Herschbach, Mol. Phys., 27, 159 (1974)

Address: Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680

TH7.   (3:30)

MEASURES OF THE SMALL CORE-VALENCE AND CORE-CORE CORRELATION ENERGY ERRORS IN THE OPTIMIZED VALENCE CONFIGURATIONS (OVC) METHOD OF DAS AND WAHL

Daniel D. Konowalow

The OVC version [1] of the multiconfiguration self consistent field approach in ab initio quantum-mechanical computations of small molecules has met with a reasonable measure of success. Even when pushed to the hilt (as we have attempted to do for low-lying states of Li_2, for example [1]), the OVC scheme gave potential curves which were slightly misshapen (ω_e and B_e too small, for example). Effective core potential computations [2] and very refined spectroscopic observations [3,4] help to understand and quantify those small defects.

[1]G. Das and A.C. Wahl, J. Chem. Phys. 47, 2934 (1967).

[2]D.D. Konowalow and M.L. Olson, J. Chem. Phys. 71, 450 (1979).

[3]D.D. Konowalow and J.L. Fish, Chem. Phys. (in press).

[4]K.K. Verma, M.E. Koch and W.C. Stwalley, J. Chem. Phys. 78, 3614 (1983).

[5]J. Verges, R. Bacis, B. Barakat, P. Carrot, S. Churassy and P. Crozet, Chem. Phys. Lett. 98, 203 (1983).

Address of Konowalow: Department of Chemistry, State University of New York at Binghamton, Binghamton, NY 13901.

TH8.   3:42

CALCULATION OF RADIATIVE TRANSITION PROBABILITIES IN THE $B^1\Pi_u - X^1\Sigma_g^+$ BANDS OF Li$_2$ AND Na$_2$

W. T. ZEMKE, J. T. BAHNS, W. T. LUH and W. C. STWALLEY

Using accurate hybrid potential energy curves and ab initio transition moment functions[*], we have calculated absolute radiative transition probabilities for the $B^1\Pi_u(v') \rightarrow X^1\Sigma_g^+(v'')$ bands of Li$_2$ and Na$_2$. In the case of Li$_2$, v" runs from $0 \rightarrow 35$ and v' runs from $0 \rightarrow 17$; v' $= 14 - 17$ levels are above the dissociation limit due to the existence of a maximum (500-600 cm^{-1}) in the potential curve at about 6 Å. In the case of Na$_2$, v" runs from $0 \rightarrow 60$ and v' runs from $0 \rightarrow 34$; v' $= 27 - 34$ levels are above the dissociation limit due to the existence of a maximum (400-500 cm^{-1}) in the potential curve at about 7 Å.

Comparisons of calculated and experimental intensities will be presented. An analysis of how these results help determine the barrier heights in the $B^1\Pi_u$ states will also be presented.

[*] D. D. Konowalow, M. E. Rosenkrantz and D. S. Hochhauser, J. Mol. Spectrosc. 99, 321 (1983).

Address of Zemke: Department of Chemistry, Wartburg College, Waverly, Iowa 50677.
Address of Bahns, Luh and Stwalley: Iowa Laser Facility and Department of Chemistry, University of Iowa, Iowa City, Iowa 52242.

TH9.   (1:53)

COMPUTATIONAL CHEMISTRY AT NASA AMES RESEARCH CENTER: AN ACTIVITY INITIATED WITH HELP AND INSPIRATION FROM A. C. WAHL

J. O. Arnold (Presented by Winifred M. Huo)

Computational Chemistry began at NASA Ames Research Center in 1971 with the help of Dr. A. C. Wahl and several other emminent quantum chemists. This effort has flourished for more than a decade because of our ability to predict observable physical properties of molecules from first principles. This heritage is briefly recounted and a summary of the group's recent activities is presented.

Topics in the summary include:

1. Results of ab initio calculations and properties derived from them for several diatomics important in entry physics studies for a new class of NASA's space vehicles (to fly in the 1988 to 2000 time frame) and for photodiagnostics of gases in cold aerodynamic flows and combustion environments.

2. Recent results on hydrocarbon species of interest for studies of combustion.

3. Ab initio studies of large clusters of transition metal atoms in the presence of H, O and CO relating to the nature of chemisorption and understanding mechanisms involved in catalysis and hydrogen embrittlement.

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Address of Huo:
Univeristy of Notre Dame, IN 46556
Mailing Address: NASA-Ames Research Center Moffett Field, CA 94035

TH10. (4:16)

ANHARMONIC VIBRATIONAL ANALYSES OF AB INITIO POTENTIAL ENERGY SURFACES FOR FORMALDEHYDE

L.B. HARDING AND W.C. ERMLER

A computer program for calculating vibrational-rotational spectroscopic constants for polyatomic molecules has been developed. Calculated energies at chosen geometries are fitted to a polynomial function of the internal coordinates which is used in a normal mode analysis. The energy surface is re-expanded as a power series in the normal coordinates with the resulting force constants then employed to incorporate the effects of anharmonicity in calculating spectroscopic constants. Formaldehyde and its deuterated isomers was examined using ab initio techniques at the self-consistent field, Møller-Plesset perturbation theory, and configuration interaction levels of approximation. Harmonic frequencies are in good agreement with experimentally derived values for the most accurate surfaces and anharmonic spectroscopic constants compare well with values recently derived from spectral data.

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Address of Ermler: Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030.

TH11. (4:28)

RELATIVISTIC AND CORRELATION CONTRIBUTIONS TO THE 2s3p SINGLET-TRIPLET INVERSION IN THE BERYLLIUM ISOELECTRONIC SEQUENCE

Y.-K. KIM AND A. W. WEISS

The inversion of the ^3P, ^1P terms of the 2s3p configurations of beryllium-like ions is well-known in atomic spectroscopy. This anomaly has been explained as due to the strong 2p3s configuration interaction as the latter configuration 'plunges' into the discrete spectrum along the isoelectronic sequence.[1]

A quantitative understanding of the ^3P - ^1P separation along the isoelectronic sequence, however, requires an adequate treatment of both correlation and relativistic effects, and we discuss here the subtle interplay of these two effects. For low stages of ionization, correlation is important for determining the level separation, while for higher stages of ionization, a correlated relativistic treatment becomes essential. The relativistic transformation to jj-coupling leads to the lowest state becoming predominantly ^3P in character by Ar^{+14}. For very highly stripped ions, relativistic effects are so dominant that the second state is no longer 2s3p but $2p_{1/2}3s_{1/2}$.

. H. Odabasi, J. Opt. Soc. Am. 59, 583 (1969).

Address: National Bureau of Standards, Washington, D.C. 20234

TH12. (4:45)

MONTE CARLO LIQUID WATER SIMULATIONS WITH FOUR-BODY INTERACTIONS INCLUDED

J. DETRICH, G. CORONGIU AND E. CLEMENTI

We have added a four-body interaction term to previously derived two- and three-body interactions for water molecules. All interactions are derived from fits to ab initio molecular calculations. Metropolis-Monte Carlo liquid simulations using these interactions are presented. Our results indicate that four-body interactions are significant.

Address of Detrich, Corongiu and Clementi: IBM Corporation, IS/TG, Department D55/Building 701, P.O. Box 390, Poughkeepsie, New York 12602

TH13.   (5:02)

CALCULATED THERMAL AND VIBRATIONALLY EXCITED RATE CONSTANTS FOR $O(^3P) + H_2$, D_2, AND HD

A. F. Wagner, J. M. Bowman, and G. C. Schatz

Transition state theory (TST), quasiclassical trajectories (QCT), and exact quantum (EQ) dynamics have been used to characterize the rate constants of $O(^3P) + H_2$ and its isotopic analogues. Two different potential energy surfaces have been used. The first is a collinear ab initio POLCI surface which incorporates the zero point energy for the bending vibration. The second is the Johnson and Winter LEPS surface. TST, QCT, and EQ calculations on the collinear portions of each surface have resulted in collinear transmission coefficients which then modify the fully dimensional TST at the calculated saddle point. For the POLCI surface, the bending degree of freedom includes the Renner–Teller effect. The resulting POLCI rate constants are extensively and favorably compared to experiment. The LEPS rate constants in terms of isotope effects are compared to fully dimensional QCT and distorted wave quantum rate constants. The fully dimensional QCT isotope effects for HD are anomalously high and suggest fundamental differences in the way classical and quantum dynamics treats bending degrees of freedom along the reaction path.

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Address of Bowman: Illinois Institute of Technology, Chicago, IL 60616.
Address of Schatz: Northwestern University, Evanston, IL 60201.

                                                                         (5:14)
TH14

THE BONDING, CHARGE DISTRIBUTION AND DIPOLE MOMENT OF THE LOW LYING STATES OF CH_2Li_2

AILEEN ALVARADO AND JAMES F. HARRISON

The electronic structure of the lowest singlet and triplet states of CH_2Li_2 has been studied with the goal of understanding the bonding in this unusual molecule. Previous work by Laidig and Schaefer[1] placed the lowest triplet approximately 2 kcal/mole above the lowest singlet with the calculated dipole moment of the singlet being +5.42 debyes and that of the triplet being -0.76 debyes. We have constructed MCSCF functions at the optimal SCF geometry and predict a similar shift in the dipole moment in going from the singlet to the triplet state. In addition these MCSCF calculations suggest an orbital interpretation of the bonding consistent with the dipole moments. Density difference plots, orbital contours and population analysis of the various MCSCF functions will be presented.

W. Laidig and H. Schaefer III, J. Am. Chem. Soc. 100, 5972 (1978).

Address of Alvarado and Harrison: Department of Chemistry, Michigan State University, East Lansing, MI   48824-1322   USA

WE1.   (1:30)

COMPARISON BETWEEN THEORY AND EXPERIMENT FOR EXCITED STATES OF MOLECULAR HYDROGEN

K. DRESSLER

The excited $^1\Sigma_g^+$ states of the H_2 molecule are affected by strong nonadiabatic coupling. The interaction of the doubly excited $1\sigma_u^2$ configuration with the Rydberg configurations $1\sigma_g$ $n\ell\sigma_g$ gives rise to the double-minimum electronic energy curves of the states EF ($2s\sigma_g$, $2\ ^1\Sigma_g^+$), GK ($3d\sigma_g$, $3\ ^1\Sigma_g^+$), and to the higher lying curves of the states i $^1\Sigma_g^+$ (i=4, 5, ...) which continue the $ns\sigma$ and $nd\sigma$ series. The vibrations of all of these adiabatic states $|i\rangle$ are mutually coupled via the operators $\langle i|d^2/dR^2|j\rangle + 2\langle i|d/dR|j\rangle d/dR$ which have been computed by Wolniewicz using ab-initio wavefunctions (i,j) = (2,3) and (3,4), and by Quadrelli using an approximate diabatic model for the entire $ns\sigma$ and $nd\sigma$ Rydberg series interacting with $1\sigma_u^2$.

The discrepancies between the nonadiabatic ab-initio results and experimental term values increase with vibrational excitation energy from $2cm^{-1}$ for EF(v=0) to $50cm^{-1}$ for GK(v=5) and they can be apportioned approximately to (a) convergence errors of the adiabatic potential energy curves (up to $\approx 20cm^{-1}$) and (b) nonadiabatic shifts caused by the higher states i > 4 (up to $\approx 30cm^{-1}$). This has been investigated with the aid of Quadrelli's model as well as by comparing the ab-initio results for H_2 and D_2. For the v=0 level of the EF state the nonadiabatic energy shift is smaller than $0.1cm^{-1}$; the $2cm^{-1}$ error of the adiabatic calculation is of magnitude comparable to ab-initio results on other excited states of H_2.

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WE2.   (2:03)

SCALAR AND VECTOR COLLISIONAL INTERFERENCE EFFECTS IN THE VIBRATION ROTATION SPECTRA OF HD AND H_2

R. M. Herman

An interference between certain components of dipole moment transition amplitudes as induced through collisions is found to be phase-correlated with those induced through subsequent collisions of the same HD molecules with foreign gas atoms. This interference leads to collisionally induced sharp spectral features having shapes which arise in a manner similar to Ramsey double resonance. These features, which depend only upon scalar functions of intermolecular displacements, will be compared with quite differently appearing features in the vibration-rotation spectrum of H_2 arising from an intercollisional interference between dipoles generated in successive collisions associated with vector functions of the intermolecular displacements. Comparison with experiment will be made, and ramifications of the vector intercollisional interference mechanism in Raman spectroscopy will be discussed.

Address: Department of Physics, The Pennsylvania State University,
          University Park, Pennsylvania 16802

WE3.   (2:36)

INTERFERENCE EFFECTS IN THE INFRARED SPECTRUM OF HD

A.R.W. MCKELLAR, J.W.C. JOHNS, W. MAJEWSKI, AND N.H. RICH

Interference between the small permanent dipole moment of HD and the dipoles induced during collisions with other molecules causes strange effects in the spectrum. The dipole P- and R-branch lines show asymmetric (Fano) line shapes, as well as anomalous intensities which vary with pressure.[1-6]

We have performed a new series of experiments on the fundamental (≈ 3700 cm^{-1}) and pure rotational (far-infrared) bands for both pure HD and HD-rare gas mixtures. The results reconcile the apparently contradictory earlier observations of destructive[1,3,6] and constructive[2] interference: in all the cases we have analyzed so far, there is initial destructive interference proportional to the density squared (and due to intracollisional effects), and, at higher pressures, eventual constructive interference proportional to the density cubed (and due to intercollisional effects). The theoretical formulation of Herman et al.[4,5] is strikingly confirmed, but no predictions are yet available for the actual values of the ("phase shift") parameters which we derive experimentally, and particularly for their variation with perturbing gas and with HD transition.

[1] A.R.W. McKellar, Can. J. Phys. 51, 389 (1973).

[2] J.D. Poll, R.H. Tipping, R.D.G. Prasad, and S.P. Reddy, Phys. Rev. Lett. 36,248 (1976).

[3] R.H. Tipping, J.D. Poll, and A.R.W. McKellar, Can. J. Phys. 56, 75 (1978).

[4] R.M. Herman, Phys. Rev. Lett. 42, 1206 (1979).

[5] R.M. Herman, R.H. Tipping, and J.D. Poll, Phys. Rev. A 20, 2006 (1979).

[6] J.B. Nelson and G.C. Tabisz, Phys. Rev. A 28, 2157 (1983).

Address of McKellar, Johns, and Majewski: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

Address of Rich: Department of Physics, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X7, Canada.

WE4.   (3:15)

THE PURE ROTATIONAL SPECTRUM OF HD: INTRACOLLISONAL INTERFERENCE AND DETERMINATION OF THE PERMANENT DIPOLE MOMENT

G.C. TABISZ

The intensity of the pure rotational absorption spectrum of gaseous HD is measured as a function of density for pure HD and HD-He and HD-Ar mixtures at 295K. The decrease in the absorption coefficient with increasing density is consistent with a destructive intracollisional interference between transitions involving the permanent and collision-induced dipole moments. The permanent dipole moment of the molecule in its ground vibrational state is found to be J dependent and in the range $(8-10) \times 10^{-4}$ D.

Dept. of Physics, University of Manitoba, Winnipeg, Manitoba, Canada, R3T 2N2

WE5.   (3:38)

THE FAR INFRARED SPECTRUM OF H_2 AND H_2 IN MIXTURE WITH He: EXPERIMENT AND THEORY*

L. FROMMHOLD AND G. BIRNBAUM

The far infrared spectra of H_2, and H_2 in mixtures with He, have been measured at a variety of temperatures from 77K to room temperature and from about 30 cm^{-1} to almost 2000 cm^{-1} for hydrogen. These spectra have been analyzed with the BC semi-empirical line shape model,[1] and the various induced dipole components have been resolved. More recently, an exact quantum mechanical formalism of the line shape problem has been developed.[2,3] Excellent agreement with experimental spectra has been obtained using ab initio[4] and empirical induced dipole models and modern refined potential functions. These calculations show the importance of dimers and pre-dissociating molecules in the collision-induced spectra of H_2, even at temperatures as high as 120K, the temperature of Jupiter's upper atmosphere.

Finally, from comparisons of the semi-empirical BC model line shape with quantum mechanically computed (QMC) shapes it is shown that the parameters in this model are accurately given by simple relations involving the first three spectral moments. Expensive quantum line shape computations may thus be replaced by the BC model, with parameters derived from relatively simple moment calculations.[5]

*Supported by the National Science Foundation, grant AST-8310786.
[1]G. Birnbaum and E.R. Cohen, Canad. J. Phys. 54, 593 (1976).
[2]G. Birnbaum, S.I. Chu, A. Dalgarno, L. Frommhold, E.L. Wright, Phys. Rev. A29, 595 (1984).
[3]G. Birnbaum, B. Guillot, and S. Bratos, Adv. Phys. Chem. 51, 49 (1982).
[4]W. Meyer and J. Schaefer, in press.
[5]A. Borysow, M. Moraldi, L. Frommhold, JQSRT, in press.

Address of Birnbaum: National Bureau of Standards, Washington, D.C., 20234.
Address of Frommhold: Physics Department, University of Texas at Austin, Texas, 78712.

WE6.   (4:11)

CHARGE INDUCED EFFECTS IN THE SPECTRA OF SOLID DEUTERIUM

J. D. POLL

Experiments will be described in which solid deuterium is irradiated by a 15 MeV proton beam. The charges created by the beam give rise to "charged induced absorption" in the infrared spectrum of deuterium. This effect will be discussed in some detail. In addition, absorption in the IR and UV is observed which appears to be due to localized electrons, either in traps or in the form of small polarons. The growth and decay of these spectral features can be studied after switching the beam on or off. It is found that the charges created in the crystal by the beam are, at sufficiently low temperature, very long lived.

Address of Poll: Guelph-Waterloo Program for Graduate Work in Physics, University of Guelph Campus, Guelph, Ontario, Canada, N1G 2W1.

WE7.   (4:24)

COLLISION-INDUCED VIBRATIONAL ABSORPTION IN THE HYDROGENS*

S. P. REDDY

Collision-induced infrared absorption spectra of H_2 and D_2 in their fundamental, first and second overtone regions and of HD in its fundamental region obtained under a variety of experimental conditions will be presented. Analyses of the absorption profiles carried out by assuming appropriate line shapes and half width parameters will be given. Collision-induced mechanisms involving electron overlap induction, quadrupolar induction, hexadecapolar induction, intercollisional interference, and intracollisional interference will be discussed. Various parameters of the colliding molecular pairs derived from the observed spectra will be presented.

Address: Department of Physics, Memorial University of Newfoundland, St. John's, Newfoundland, Canada, A1B 3X7

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THEORY FOR VIBRATION-ROTATION-LARGE AMPLITUDE MOTION INTERACTIONS

Yuhua Guan and C. Richard Quade

A theory for vibration-rotation-large amplitude motion interactions is being developed using curvilinear internal coordinates for the vibrational degrees of freedom. Last year we presented results on the zeroth order separations of vibration from rotation and of the LAM from the other vibrations. Now a Van Vleck transformation through second order has been used to obtain the effective Hamiltonian for the rotation-LAM interactions that has the form

$$H^{eff}_R = H^O_\tau + H'_\tau + \sum H'_{\tau,k}(v_k + 1/2) + H^O_R + H'_R$$
$$+ \sum H'_{R,k}(v_k + 1/2) + H^O_{\tau R} + H'_{\tau R}$$
$$+ \sum H'_{\tau R,k}(v_k + 1/2) + H_{CD} .$$

All primed terms arise from the interaction with the other vibrations. The geometry dependent coefficients have been calculated for non-linear XY_2 molecules. Applications are underway for H_2O, treating the bending mode as a large amplitude motion.

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INTERNAL COORDINATE FORMULATION FOR THE VIBRATION-ROTATION ENERGIES OF POLYATOMIC MOLECULES. TETRAHEDRAL AND OCTAHEDRAL SPHERICAL TOP MOLECULES

William B. Clodius and C. Richard Quade

The theory of vibration-rotation interactions in tetrahedral and octahedral spherical top molecules has been developed using curvilinear internal coordinates for the vibrational degrees of freedom. Integral to the development has been a derivation of the vibrational kinetic energy for configurations away from equilibrium when redundant coordinates are present in the symmetry coordinate basis. General expressions for the inertial coefficients, Coriolis coupling coefficients, and vibrational kinetic energy anharmonicity coefficients have been derived for both the tetrahedral and octahedral molecules. A Van Vleck transformation is used to obtain both the diagonal and off-diagonal theoretical vibration-rotation and vibration anharmonic spectroscopic coefficients to second order. Comparisions with the earlier work on methane by Gray and Robiette are good. Application is made in the partial determination of the anharmonic potential energy coefficients for SF_6 and CF_4. As has been found in our previous work, the curvilinear internal coordinate approach has definite advantages over the Cartesion displacement coordinate approach for the angle bending modes.

Gray and Robiette, Molecular Physics 37, 1901(1979).

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WF3.   (2:49)

RELATING ALTERNATIVE FORMULATIONS OF ASYMMETRIC-ROTATOR HAMILTONIANS WRITTEN IN TERMS OF CYLINDRICAL-TENSOR ANGULAR-MOMENTUM OPERATORS

PAUL M. PARKER

Effective rotational Hamiltonians, written as power series in the body-fixed angular momentum components P_α (α = a, b, c), have been used extensively in the analysis of high-resolution pure rotation and vibration-rotation spectra. When written in terms of cylindrical tensor components, two alternative forms are in use.[1] In one form, the operators are constructed as Hermitian combinations of products of integral powers of P^2, P_c^2 and $(P_a^2 - P_b^2)$ where $P^2 = P_a^2 + P_b^2 + P_c^2$, and for the other form one uses integral powers of P^2 and P_c^2 along with $(P_+^{2n} + P_-^{2n})$, n = 1, 2, 3, ... where $P_\pm = P_a \pm iP_b$. Since $(P_a^2 - P_b^2)^n \neq (P_+^{2n} + P_-^{2n})/2^n$ except for n = 1, the sets of empirical constants determined with the two formulations will not, in general, be identical and the differences become the more extensive the larger the value of n. Since coefficients of octic, dectic and even higher powers of angular momentum are now regularly reported, it becomes important that the implications of the above inequality be examined in detail so that results from different laboratories can be compared more readily and so that empirical constants can be correctly related to theoretical expressions and reduction-invariant combinations which are specified through a model Hamiltonian written in terms of Hermitian combinations of products of integral powers of P_a^2, P_b^2 and P_c^2.

A study of the above inequality will be described and its consequences for rotational Hamiltonians in general will be illustrated with a detailed consideration of quartic Hamiltonians.

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[1] J. K. G. Watson in "Vibrational Spectra and Structure" (J. R. Durig, Ed.), Vol. 6, pp. 1-89, Elsevier, New York, 1977.

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WF4.

GROUP THEORETICAL TREATMENT OF THE PLANAR INTERNAL ROTATION PROBLEM IN $(HF)_2$

JON T. HOUGEN AND NOBUKIMI OHASHI

The $(HF)_2$ dimer is believed to exhibit an internal rotation tunneling process between two planar but nonlinear equilibrium configurations, during which tunneling the roles of the hydrogen-bonded and the free hydrogen atoms are interchanged. This process can be represented schematically with labeled atoms as $H_1F_aH_2F_b = F_aH_1F_bH_2$, and gives rise to a permutation-inversion group G_4 containing four operations. In the present work the vibration-rotation-tunneling problem in $(HF)_2$ has been treated group theoretically in three ways: (i) by allowing tunneling only through a trans planar C_{2h} intermediate, (ii) by allowing tunneling only through a cis planar C_{2v} intermediate, and (iii) by considering the trans and cis tunneling processes to both occur, though not necessarily to the same extent. The several molecular symmetry groups used in these treatments are: (i) the point group C_{2h}, (ii) the point group C_{2v}, and (iii) a double group, which might be thought of as $G_4^+ = C_{2h}^+ = C_{2v}^+$. Nonplanar tunneling paths have not been considered, since the internal axis method (IAM) coordinate system used here cannot easily be adapted to nonplanar internal rotation motions in this molecule. Various details of energy level diagrams, symmetry species for operators, selection rules for spectroscopic transitions, and statistical weights will be presented for the $(HF)_2$ tunneling problem, as well as some speculation on the general question of the conditions under which it is preferable to use point groups, permutation-inversion groups, or double groups.

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WF5.

THE SEMIRIGID BENDER AND INTERNAL ISOMERIZATION OF HCN TO CNH

S.C. ROSS

The semirigid bender model has previously been used to study the stretching-bending vibrational levels of HCN, allowing for the internal isomerization of HCN into CNH (1). This model has now been extended to allow for the overall rotation of the molecule. The results of a fitting to the experimentally observed stretching-bending and bending-rotation levels of HCN and CNH are described.

(1) S.C. Ross and P.R. Bunker, J. Mol. Spectrosc., 101, 199-211 (1983).

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WF6. (3:45)

PREDICTION OF MANY NEW OPTICALLY PUMPED SUBMILLIMETER-WAVE LASER EMISSIONS IN CDF_3

J. P. SATTLER, R. P. LEAVITT, T. L. WORCHESKY, AND M. S. TOBIN

We predict over 300 new submillimeter-wave (SMMW) laser emission lines obtainable by the optical pumping of CDF_3 with isotopic CO_2 and N_2O lasers. These predictions are based on our measurements and analysis of the SMMW and IR spectra of the ν_5 band. Our heterodyne measurements on 22 SMMW laser emissions and 404 IR absorptions have been analyzed together with previous data to determine the molecular constants of the ground and ν_5 states.

We made SMMW heterodyne measurements by beating the optically pumped laser radiation against harmonics of a phase-locked 35-GHz klystron. We made IR heterodyne measurements by beating diode laser radiation centered on a molecular absorption against radiation from a CO_2 laser. Expressions that included ℓ-doubling and centrifugal distortion effects to the eighth power in J and K were used to fit to the data of the ground and excited states simultaneously. The effective best-fit molecular constants were obtained. Since these molecular constants were determined in large part from heterodyned data that were well calibrated with respect to absolute frequency standards, and since the frequencies of many of the various isotopic lines of CO_2 and N_2O are also well known, it was straightforward to correlate these IR laser lines with the calculated IR molecular absorption spectrum to predict the resultant pure-rotational SMMW laser emissions. Most frequencies were predicted to ~ 1 MHz uncertainty.

Energy levels for every value of J' from 1 to 56 are pumpable with these known IR lasers, so that approximate frequencies,

$$\nu \text{ (MHz)} \approx 2(J' + 1) \times 9911.6938 ,$$

are in principle obtainable from this molecule for all J' satisfying $1 \leqslant J' \leqslant 56$. The predicted laser emissions are tabulated according to frequency with the corresponding pump lines, IR absorption frequencies, and intensities; the tabulation permits potential users to evaluate the merits of the various pumping schemes corresponding to a given emission frequency.

Thus, the molecule CDF_3 provides a rich choice of SMMW laser lines at approximately 20-GHz intervals from the millimeter-wave region through 1.1 THz.

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WF7. (3:57)

THE MICROWAVE SPECTRUM OF TRIFLUOROETHYLENE OXIDE

T.T. RAW AND C.W. GILLIES

The microwave spectrum of trifluoroethylene oxide has been investigated in the region of 26.5 to 35 GHz. The molecule exhibits strong μ_b and μ_c-type transitions, as well as considerably weaker μ_a-type transitions. A centrifugal distortion analysis was carried out using 120 transitions, including R-branch transition up to J = 29 → 30 and Q-branches to J = 29. The rotational constants which were determined from an eight parameter fit are:

$$A=6669.566(2), B=3126.567(1), \text{ and } C=2652.440(1).$$

These constants are consistent with predictions based on the experimental structural trends established for other fluorinated oxiranes.

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WF8.

MOLECULAR STRUCTURE OF TRANS-1,2-DIFLUOROCYCLOPROPANE

N. CRAIG, C.W. GILLIES, H. JUSTNES, AND S. SENGUPTA

The microwave spectra of the following carbon-13 isotopes of trans-1,2-difluorocyclo-propane have been assigned in natural abundance: $^*\overline{CHFCHFCH_2}$, $\overline{CHFCHF^*CH_2}$, $^*\overline{CHFCHFCD_2}$ and $\overline{CHFCHF^*CD_2}$. Combination of these data with the normal and deuterium isotopic assignments reported previously[1] provides sufficient rotational constants to determine the molecular structure. The partial Kraitchman parameters are:

$$r_s(C_1C_2) = 1.466(4) \qquad \Theta(HCF) = 111.2(4)$$
$$r(C_{1,2}C_3) = 1.488(5) \qquad \Theta(HC_3H) = 116.8(2)$$
$$r(C_{1,2}F) = 1.383(3) \qquad \Theta(FC_1C_2) = 117.3(3)$$
$$r_s(C_{1,2}C_H) = 1.090(4) \qquad \Theta(FC_{1,2}C_3) = 118.4(3)^{\circ}$$
$$r(C_3H) = 1.083(2)\overset{\circ}{A}$$

These experimental parameters are compared to theoretical geometries and predictions of the influence of fluorine substituents upon bonding in three-membered rings.

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[1] S.K. Sengupta and V.W. Laurie, Paper MS4, 31st Symposium on Molecular Spectroscopy, Columbus, Ohio (1976).

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WF9.

MICROWAVE SPECTRUM AND MOLECULAR STRUCTURE OF CIS-1,2-DIFLUOROCYCLOPROPANE

N. CRAIG, C.W. GILLIES, H. JUSTNES, AND S. SENGUPTA

The microwave spectrum of a carbon-13 isotope of cis-1,2-difluorocyclopropane, $^*\overline{CHFCHFCH_2}$, has been assigned in natural abundance. The normal and deuterium isotopic rotational constants reported previously[1] were combined with the carbon-13 data to partially determine the molecular structure. The r_s parameters are $r(C_1C_2) = 1.488(3)\overset{\circ}{A}$ and $r(C_{1,2}H) = 1.093(4)\overset{\circ}{A}$. These structural parameters will be compared to the trans isomer of 1,2-difluorocyclopropane as well as to related geometrical pairs of fluorinated three-membered rings. The results will also be discussed in terms of recent theoretical studies of these ring systems.

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[1] S.K. Sengupta and V.W. Laurie, Paper TGS, 32nd Symposium on Molecular Spectroscopy, Columbus, Ohio (1977).

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WF10.

MICROWAVE SPECTRA AND MOLECULAR STRUCTURE OF <u>CIS</u>, <u>TRANS</u>-1,2,3-TRIFLUOROCYCLOPROPANE

R.N. BEAUCHAMP, J.W. AGOPOVICH, AND C.W. GILLIES

The microwave spectrum of <u>cis,trans</u>-1,2,3-trifluorocyclopropane was investigated in the region of 26.5 to 40.0 GHz. Assignments of the μ_a and μ_c type R-branch transitions were made for the normal isotopic species and five deuterated species[1], as well as the four carbon-13 isotopic species: ^{13}CHFCHFCFH, CHFCHF ^{13}CFH, ^{13}CDFCDFCFD, CDFCDF ^{13}CFD. R_0 and partial-R_s structures were obtained in both the normal isotopic species and the d_3-isotopic species framework. The preponderance of data enabled the calculation of a small hydrogen coordinate in a variety of ways, including the use of Kraitchman's and Chutjian's equations as well as Pierce's double substitution method. Structural parameters resulting include:

$$r(C_1C_2) = 1.477(6) \overset{o}{A} \qquad r(C_1F) = 1.387(4) \overset{o}{A}$$
$$r(C_2C_3) = 1.500(3) \overset{o}{A} \qquad r(C_2H) = 1.075(6) \overset{o}{A}$$
$$r(C_1H) = 1.085(4) \overset{o}{A} \qquad r(C_2F) = 1.368(8) \overset{o}{A}$$
$$\Theta(HC_1F) = 114.7(6)^o$$
$$\Theta(HC_2F) = 109.3(8)^o$$

where C_1 is the carbon in the ac-symmetry plane. The structure obtained will be discussed in light of experimental and theoretical work on similar systems.

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[1] J.W. Agopovich, Paper RB7, 37th Symposium on Molecular Spectroscopy, Columbus, Ohio (1982).

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WG1.

TRANSITION-METAL DIATOMICS; ScNi, TiCo, TiV, VNi

R.J. VAN ZEE AND W. WELTNER, JR.

These molecules were formed during the trapping of the vaporized metal atoms in argon matrices at 4°K. Analysis of their X-band ESR spectra show that the electronic ground state of the iso-electronic ScNi and TiCo molecules is $^2\Sigma$. TiV and VNi were found to have $^4\Sigma$ ground states with zero-field-splitting parameters $D > 1$ cm^{-1}. Hyperfine splittings produced by the ^{45}Sc, ^{47}Ti (enriched), ^{51}V, and ^{59}Co nuclei provide evidence as to the unpaired electronic configurations and suggest multiple metal-metal bonding in all cases. Their properties will be discussed relative to other first-row transition-metal diatomics.

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WG2.

LiCr AND NaCr MOLECULES

R.J. VAN ZEE, C.A. BAUMANN AND W. WELTNER, JR.

ESR spectra of LiCr and NaCr trapped in argon matrices at 4°K were observed centered around $g = 2$. The five fine-structure transitions of a $^6\Sigma$ molecule were observed in each case but with no alkali-metal hyperfine structure. The zero-field-splitting parameter $|D|$ was 0.065 and 0.050 cm^{-1} in the lithium and sodium molecules, respectively. Comparison with the HCr molecule[1] will be made. Attempts to observe the corresponding LiMn and NaMn molecules were without success.

[1] R.J. Van Zee, T.C. DeVore, and W. Weltner, Jr., J. Chem. Phys. 71, 2051 (1979).

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WG3.   (2:44)

THE GENERATION AND TRAPPING OF HIGH TEMPERATURE CATION RADICALS IN NEON MATRICES AT 4K: ESR AND AB INITIO CI INVESTIGATION OF $^{28}SiO^+$ and $^{29}SiO^+$. LON B. KNIGHT, JR., ANDREW LIGON, E. R. DAVIDSON, DAVID FELLER, JR.

The molecular cation radicals $^{28}SiO^+$ and $^{29}SiO^+(^2\Sigma)$ have been generated during neon matrix deposition by the high temperature vaporization of $SiO_2(s)$ and $SiO(s)$ under ionizing conditions. Both open-tube neon discharge photoionization and electron bombardment ionization techniques were utilized. Both methods have been previously applied to volatile compounds but not to refractory substances.[1,2] Nuclear hyperfine structure, reflecting s and p orbital character, for $^{13}C^{17}O^+$ is compared with similar findings for $^{29}SiO^+$ in order to monitor the electronic structure changes that occur as silicon replaces carbon in a "simple" diatomic radical.

Ab initio CI calculations of the isotopic and dipolar nuclear hfs of ^{29}Si in $^{29}SiO^+$ showed excellent agreement with experimental results provided the orbitals were carefully defined with the use of an iterative natural orbital (INO) selection process. The SiO^+ radical is isoelectronic to the previously studied AlO radical which also required the INO approach for calculating one electron properties such as nuclear hf parameters. The electronic structure of SiO^+ was observed to be significantly different from that of CO^+.

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[1] Lon B. Knight, Jr. and J. Steadman, J. Chem. Phys. 77, 1750 (1982).

[2] Lon B. Knight, Jr., J. M. Bostick, R. W. Woodward and J. Steadman, J. Chem. Phys 78, 6415 (1983).

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WG4.   (2:56)

ESR SPECTRA OF MATRIX ISOLATED LiO$_2$

D. A. GARLAND AND D. M. LINDSAY

ESR spectra have been obtained for LiO_2 trapped in krypton and nitrogen matrices, and are consistent with an ionic model, $Li^+O_2^-$, of C_{2v} symmetry. Each spectrum has a triplet structure arising from the three principle values of the g-tensor. In Kr, the values are $g_{zz}=2.0570$, $g_{xx}=2.0095$ and $g_{yy}=2.0024$. For the N_2 matrix, $g_{zz}=2.0667$ and $g_{xx}=2.0080$ (g_{yy} was not determined because of overlap with intense N atom transistions centered at $g=2.0014$). The g_{zz} transistion in N_2 has a well resolved hyperfine quartet structure arising from ^7Li (I=3/2), with $a_{zz}=2.33G$, and the g_{yy} transistion in Kr has $a_{yy}=2.65G$. Hyperfine structure was not resolved for g_{xx} in either matrix. An apparent but poorly resolved quadrupole interaction is observed for $g_{zz}(N_2)$ and $g_{yy}(Kr)$.

The alkali cation lifts the degeneracy of the O_2^- HOMO and splits it into an in plane orbital, $\pi_x^*(b_1)$, and an out of plane orbital, $\pi_y^*(a_2)$. The splitting parameter between the two orbital, δ, decreases down the series NaO_2, KO_2, RbO_2, then increases for $CsO_2(1)$. δ is inversely proportional to Δg_{zz}, the shift from the free electron g value. The g_{zz} values for LiO_2 support the "inversion model" for CsO_2 where the ground state configuration changes from $^2A_2$ to $^2B_1$.

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(1) D.M.Lindsay, D.R.Herschbach, and A.L.Kwiram, Chem. Phys. Let. 25, 175 (1974).

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WG5.   (3:13)

NONPHOTOCHEMICAL HOLE BURNING, SITE INTERCONVERSION AND ISOSBESTIC BEHAVIOUR OF
RESORUFIN IN PMMA   A. F. Childs and A. H. Francis

Nonphotochemical hole burning (NPHB) has been investigated for the ionic dye resorufin
in polymethylmethacrolate (PMMA)[1]. It has been possible to burn relatively deep holes in
the innomogeneously broadened electronic origin and vibronic features of the basic form of
the dye. Optical density changes at the burn frequency are typically 0.35 and the zero-
phonon holes are accompanied by phonon and "pseudophonon" sidebands. Spectral changes
associated with the energetically displaced absorbers were also observed. The non-
photochemical nature of the hole burning process has been demonstrated by laser induced
hole refilling [2] which has been shown to occur over energy differences in excess of 100 cm^{-1}.
The temperature dependence of the hole linewidth was found to be proportional to $T^{1.3}$,
consistent with previous observations of holes burned in polymer matrices.

An unusual feature of the hole spectra is the appearance of an isosbestic point (a
point of optical invariance) in both the hole burning and hole annealing spectra. Isosbes-
tic behavior may be characteristic of NPHB at relatively high laser powers (100 mw/cm^2).
The relationship between isosbestic behavior in NPHB and spectral-diffusion line broadening
will be discussed.

[1] A. P. Marchetti, M. Scozzafava, R. H. Young, Chem. Phys. Lett. 51, 424 (1977).
[2] J. M. Hayes, G. J. Small, Chem. Phys. Lett. 54, 435 (1978).

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WG'1.   (3:40)

MECHANISMS AND RATE CONSTANTS FOR THE VIBRATIONAL RELAXATION OF HD(v=4, 5, and 6) IN COLLISIONS
WITH HD, He, AND D_2

J. GELFAND, R.B. MILES, E.A. ROHLFING AND H. RABITZ

The relaxation of highly vibrationally excited HD with several collision partners is examined
using direct overtone excitation and time-resolved photoacoustic detection of the subsequent change
in translational energy of the gas. Analysis of such data for HD(v=4, 5, and 6) self-relaxation
yields vibration-translation (V-T) and vibration-vibration (V-V) rate constants for collisions be-
tween HD(v=1 to 6) and HD(v=0). The V-T rates become larger than the V-V rates above v=4. Similar-
ly, relaxation data for the HD(v=4 and 5)-^{4}He systems is analyzed and the HD-^{4}He V-T rate constants
at v=4 and v=5 are presented. The differences in the quantum number scaling of the V-T rates for
the HD-HD and HD-^{4}He systems are discussed. Finally, the time-resolved photoacoustic data for
HD(v=4) relaxing in collisions with D_2 shows the effect of the rapid, near-resonant V-V energy trans-
fer between HD in the v=1 through v=4 levels and D_2 in V=0.

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WG'2.

ENERGY TRANSFER PATHWAYS FOR $A^2\Delta$ CH IN AN ATMOSPHERIC PRESSURE FLAME[*]

NANCY L. GARLAND AND DAVID R. CROSLEY

Vibrational energy transfer (V) and rotational energy transfer (R) within the $A^2\Delta$ state of CH has been studied in an atmospheric pressure CH_4/O_2 flame at ~2000 K. A laser pumps specific N' levels in v'=0 and fluorescence in the (1,0) and (0,0) bands is monitored. Excitation of N'=5 (E_N ~400 cm^{-1}) shows a partially rotationally relaxed distribution within v'=0 and very little v'=1 emission (ΔG ~2700 cm^{-1}); excitation of N'=13 (E_N ~2500 cm^{-1}) produces considerable transfer to v'=1 but less rotational redistribution than for the low rotational level. A more extensive map of relative R, V, and electronic quenching routes as a function of N' is in progress.

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WG'3.

ROTATIONAL-STATE SPECIFIC ELECTRONIC QUENCHING OF OH $(A^2\Sigma^+, v'=0)$[*]

RICHARD A. COPELAND, MARK J. DYER AND DAVID R. CROSLEY

Electronic quenching rate constants for collisions of OH $(A^2\Sigma^+, v'=0)$ with a variety of collision partners were measured for individual rotational levels using laser-induced fluorescence. Colliders studied to date are H_2O, O_2, N_2, H_2, D_2, CH_4, D_2O, N_2O, SF_6, CF_4 and CCl_4. The large rotational energy spacing, along with the generally rapid electronic quenching of OH, permitted the extraction of these rotation-state-specific rate constants from the pressure dependence (0-100 mtorr) of the temporal evolution of the total fluorescence.

There exists a significant decrease (up to 60% for N'=7 compared to N'=0) in electronic quenching with increasing rotational level for most collision partners, even though the absolute magnitude of the rate constant varies more than a factor of 30 over the set. SF_6 and CF_4 are inefficient electronic quenchers but efficient at rotational energy transfer, masking any rotational level effect. The substitution of D_2 for H_2 and D_2O for H_2O, thereby changing the vibrational and rotational structure of the quencher, caused a negligible change in the quenching cross sections. Collisions of $OD(A^2\Sigma^+, v'=0)$ with D_2O show similar effects.

This effect was first observed by McDermid and Laudenslager for N_2 and O_2.[1] Its persistence throughout the numerous collision partners suggests that electronic energy transfer in this system, where long range forces are important,[2] is sensitive to dynamical effects caused by the internal state of the OH which is quenched in the collision.

[1] I. S. McDermid and J. B. Laudenslager, J. Chem. Phys. **76**, 1814 (1982).
[2] P. W. Fairchild, G. P. Smith, and D. R. Crosley, J. Chem. Phys. **79**, 1795 (1983).

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WG'4.   (4:31)

INTERSYSTEM COLLISIONAL TRANSFER OF EXCITATION AMONG THE TRIPLET STATES OF MOLECULAR

NITROGEN   W. BENESCH and D. FRAEDRICH

We have undertaken a series of investigations to attain an understanding of the role of collisions in the determination of the relative populations of the excited states of molecular nitrogen in electric discharges. Earlier, we had noted that emission originates in vibrational levels of these electronic states which would be populated only very sparsely through the agency of direct electron excitation from the ground state. Furthermore, the influence of collisions is underscored by the observed differences between N_2 emission spectra in the aurora and in the laboratory.[1]

We have found many cases among the neighboring vibrational levels of the $W\ ^3\Delta_u$, $B'\ ^3\Sigma_u^-$, and $B\ ^3\Pi_g$ states where the populations are completely equilibrated by collisions in laboratory discharges down at least as far as the 100 milliTorr pressure range. This circumstance provides a powerful tool for quantitative spectroscopic analysis in that in a number of situations we have been able to infer unknown level populations from their collisional equilibration with known level populations.

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[1] W. Benesch, J. Chem. Phys. **78**, 2978 (1983).

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WG'5.   (4:48)

CONTINUOUS WAVE OPTICALLY PUMPED IF $B^3\pi(0^+) \rightarrow X^1\Sigma(0^+)$ LASER

S. J. DAVIS, L. HANKO, AND P. J. WOLF

A continuous wave optically pumped iodine monofluoride laser operating on the $B^3\pi(0^+) \rightarrow X^1\Sigma(0^+)$ system is described. Laser operation was achieved on a series of rotational lines originating from $v' = 2, 3, 4,$ and 5. By tuning the dye laser pump source over a single rovibronic line, spectral structure was produced on the IF laser output that ws analyzed and found to be consistent with the hyperfine structure of the B state of IF. The nuclear quadrupole coupling constant, $-eQ_mQ$, and the spin-rotation constant, C_I, were determined as (443 ± 70) MHz and (34 ± 6) kHz, respectively, for the $(v', J') = (3, 19)$ state in IF(B).

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WG'6.   (5:00)

VIBRATIONAL AND ROTATIONAL ENERGY TRANSFER IN THE $B^3\pi(0^+)$ STATE OF IF

P. J. WOLF, R. F. Shea, and S. J. Davis

Vibrational and rotational transfer rates were measured in the $B^3\pi(0^+)$ state of IF using both steady state and temporally resolved, spectrally resolved laser induced fluorescence techniques in a chemically reactive flow system. Vibrational energy transfer was studied as a function of both initially populated vibrational level ($1 < v' < 7$) and collision partner (noble gases, N_2, O_2, and F_2). Rotational energy transfer was studied in the presence of several bath gases (He, Ne, Ar, Kr, Xe). Rotational transfer ($k_R \sim 10^{-10}$ cc/sec) was found to be approximately two orders of magnitude faster than vibrational transfer ($k_v \sim 10^{-12}$ cc/sec). Comparisons of results to existing simple models will be presented.

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WH1.

EFFECTIVE HAMILTONIANS IN FOCK SPACE AND THE SIMULTANEOUS CALCULATION OF
SEVERAL ELECTRONIC STATES
(INVITED PAPER)

W. KUTZELNIGG AND S. KOCH

The Fock space Hamiltonian H - which has eigenstates of arbitrary number of
electrons in a given nuclear framework - is transformed to an effective Hamil-
tonian L, which has (in principle) the exact eigenvalues but simple model
states as eigenfunctions.[1] The method can be regarded as a non-perturbative
generalization of quasidegenerate many-body perturbation theory. It is formu-
lated in spinfree form in the framework of the unitary group. In contrast to
the MCSCF-CI method dynamical correlation is treated first and near-degeneracy
effects at the end. All interesting states are obtained from a small CI based
on L. Various states of a neutral molecule and its ions are obtained from the
same L. In the case of avoided crossings one can choose to get either adiabatic
or diabatic states. Results for spectral transition energies and ionization
potentials of atoms and small molecules are encourageing.

[1] W. Kutzelnigg, J. Chem. Phys. 77, 3081 (1982)
   W. Kutzelnigg and S. Koch, J. Chem. Phys. 79, 4315 (1983)

Adress: Lehrstuhl f. Theoretische Chemie, Ruhr-Universität, D-4630 Bochum,
Germany

WH2.

NUMERICAL WAVEFUNCTIONS - METHODS FOR THEIR CALCULATION
(INVITED PAPER)

J. Hinze

A procedure for the direct numerical calculation of Hartree-Fock functions for
molecules is given. The extension to obtain MCSCF functions will be illustrated also.
Some examples will be given for the application of the direct numerical wavefunction
methods to spectroscopic problems.

Address: Fakultät für Chemie, Universität Bielefeld, D 4800 Bielefeld, FRG.

AB INITIO CALCULATIONS INCLUDING RELATIVISTIC EFFECTS FOR THE NEUTRAL AND POSITIVE ION DIMERS OF GOLD AND SILVER

R.B. ROSS AND W.C. ERMLER

The ground electronic states of neutral and ionized diatomic silver and gold and the mixer dimer AgAu are investigated by ab initio self-consistent field and configuration interaction calculations. Relativistic effective potentials are employed to replace a defined number of core electrons in the atoms. Basis sets comprised of Slater-type functions describe the valence electrons. Electronic properties of each species are calculated and compared to experiment, other effective potential calculations and non-relativistic all-electron calculations. Bond lengths and dissociation energies for Ag_2, Au_2, and AgAu were computed at the CI level to be 2.76Å, 1.17eV, 2.66Å, 1.68eV, 2.63Å, and 2.31eV, respectively. The calculated equilibrium bond lengths are found to agree with experiment to about 0.1 Å. It is speculated that the differences between the calculated and experimental values of bond lengths are due to a lack of f-type functions and additional d- and p-type functions in the basis and the omission in the CI procedures of configurations corresponding to all double excitations out of the d shell.

Address of Ross and Ermler: Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030.

OPTO-VIBRONIC INDUCTION OF CHIRALITY AND SPIN SELECTION RULE IN JAHN-TELLER EFFECT. Ying-Nan Chiu

A mechanism is proposed for the production of chiral molecules through the co-operative action of polarized light and vibronic interaction. It requires a doubly-degenerate electronic state of an achiral molecule be splitted by a non-degenerate vibration of pseudoscalar symmetry in a Jahn-Teller Effect. The splitting results in symmetric double potential wells for the lower level, with one side of the well corres-ponding to one enantiomer and the other side to its mirror image, and with equal prob-ability for each. It will be shown that the discrimination of one enantiomer from the other may be assisted either by the neutral-current coupling to nuclear weak inter-action or by a second-order radiative interaction[1] both of which have pseudoscalar symmetry. It was found that only a limited class of molecules are amenable to this phenomenon. They belong to D_{2d}, D_{4d}, D_{6d}, S_4 and S_8. Spin singlet and doublet states are both considered. For odd-electron[2] and transformation of spin functions[3], the most general selection rule consistent with time-reversal is derived. New tabulation is given to correct some misconceptions and minor errors in existing literature.

1.
    Y.N. Chiu, J. Chem. Phys. 50, 5336 (1969)
2.
    H.A. Jahn, Proc. Roy. Soc. (London) A164, 117 (1938)
3.
    G. Herzberg "Electronic Spectra and Electronic Structures of Polyatomic Molecules" (D. Van Nostrand Co., Inc.,Prentice Hall, N.J. 1966)

Address of Chiu: Center for Molecular Dynamics and Energy Transfer, Department of Chemistry, The Catholic University of America, Washington, D.C. 20064

WH5.   (4:14)

OPTICAL ACTIVITY OF METASTABLE TWISTED ALLENES   Ying-Nan Chiu

The possibility of observing optical rotation in an
excited transient state of allene[1], $H_2C=C=CH_2$, is explored
theoretically. The optical activity is attributed to twisting
internal rotation that results in a double-minimum potential.
The electronic states involved, the molecular orbitals as well
as their correlation from perpendicular to twisted and to
planar configurations will be shown and their relevance to
optical rotation will be analyzed. The dissymmetric perturbation
that causes resolution of one of the enantiomers from a racemic
situation, without recourse to intermolecular interaction, will
be discussed. Factors such as tunneling, time scale of
interaction, induction of unsymmetrical wells, thermodynamic
effects, photon helicity and conservation of parity will be
elucidated.

1.
    Ying-Nan Chiu, J. Am. Chem. Soc. 104, 6937 (1982) and
references therein.

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Transfer, Department of Chemistry, The Catholic University of
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WH6.   (4:31)

THE ELECTRONIC STRUCTURE OF C_4*

Z. Z. WANG, R. N. DIFFENDERFER, AND I. SHAVITT

Electronic structure calculations were carried out for the C_4 molecule in the linear ($^3\Sigma_g^-$)
and rhombus (bicylic, ^1A_g) configurations. The calculations used double-zeta (DZ) and DZ plus
polarization (DZP) basis sets, and were carried out at the SCF (RHF), MCSCF, single-reference
CI, and multireference CI levels. The geometries of the two structures were optimized at the
MCSCF level, and the resulting bond lengths are greater by 0.03 - 0.09 Å than those optimized by
Whiteside et al.[1] at the SCF (UHF) level. The relative energies of the two structures are very
sensitive to the basis set used and, to a lesser degree, to the type of wave function. The DZ
basis strongly favors the linear structure, but the energies of the two structures are
comparable when the DZP basis is used.

[1]R. A. Whiteside, R. Krishnan, D. J. Defrees, J. A. Pople, and P. v. R. Schleyer, Chem.
    Phys. Letters 78, 538 (1981).

Address: Department of Chemistry, Ohio State University, Columbus, Ohio, 43210, U.S.A.
Permanent address of Z.Z. Wang: Institute of Theoretical Chemistry, Jilin University, Changchun,
China.

(4:48)

CALCULATION OF THE POTENTIAL ENERGY CURVES FOR THE LOWEST LYING ELECTRONIC STATES OF THE ISOVALENT DIATOMIC MOLECULES Si_2, Ge_2, SiC AND GeC USING AB INITIO HF-CI METHOD

H. M. NAGARATHNA (NAIK), IRENE SHIM AND K. A. GINGERICH

All electron ab-initio Hartree-Fock(HF) and configuration interaction (CI) calculations have been performed on Si_2, Ge_2, SiC and GeC molecules to predict the potential energy curves for the lowest lying electronic states. Si_2 and Ge_2 molecules show a similarity in their multiplet structure resulting in a $^3\Sigma_g^-$ ($\pi_u^2\sigma_g^2$) ground state and a $^3\Pi_u(\pi_u^3\sigma_g)$ as the first excited state with a smaller energy separation from the ground state. SiC and GeC molecules exhibit a similarity in their multiplet structure with a $^3\Pi$ ($\pi^3\sigma$) ground state and a $^3\Sigma^-$ ($\pi^2\sigma^2$) as the first excited state with an energy separation of $\simeq$ 0.8 eV from the ground state.

The spectroscopic constants have been calculated for the ground state and some of the excited states of the above molecules and compared with the available experimental data. The low lying electronic states are useful in an accurate evaluation of the dissociation energy of these molecules using mass spectrometric measurements.

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(5:30)

THEORETICAL ASSIGNMENT OF THE UV SPECTRA OF ALKYL RADICALS

M.R.A. Blomberg, B.H. Lengsfield, III, P.E.M. Siegbahn and B. Liu

ABSTRACT Ab initio SCF and CI calculations have been performed to assign the UV spectra of the ethyl, isopropyl and t-butyl radicals. Contrary to previous speculation, the low lying states are shown to be predominantly Rydberg in character. The most noteworthy feature of the UV spectra of these series of alkyl radicals, including also the methyl radical, is the red-shift obtained with increasing number of methyl groups adjacent to the radical carbon. This red-shift is explained by the increased stability of the carbonium ion core of the Rydberg states as the number of methyl groups increases. A more detailed investigation has been undertaken for the ethyl radical, for which the 3p spectrum shows a broad main peak with two small extra peaks on the long wavelength side. To interprete this part of the spectrum the stability of the 3p states toward dissociation is assessed. The small peaks are probably transitions to two bound 3p states of a non-classical structure of the ethyl radical with one hydrogen bridging the two carbons. The Rydberg states of this geometry are shown to be of lower energy than the vertical structure by an amount that corresponds to the distance between the main peak and the small peaks. The main broad peak can be understood if one of the 3p states can be shown to be dissociative and possible dissociation paths are investigated.

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COBLENTZ PRIZE AND ASSOCIATED SEMINAR OF INVITED SPEAKERS

Award of the Prize by the Coblentz Society of S. R. Leone   (8:30)

RA1.   (8:40)

SPECTROSCOPIC INVESTIGATIONS OF MOLECULAR REACTION DYNAMICS   (AWARD LECTURE)

STEPHEN R. LEONE, Joint Institute for Laboratory Astrophysics and
Department of Chemistry, University of Colorado, Boulder, Colorado,
80309, and the National Bureau of Standards, Boulder, Colorado, 80309.

RA2.   (9:25)

VIBRATIONAL STATE-DEPENDENT HYPERFINE COUPLING OF HF   Ch. Breant, T. Baer, D.
Nesbitt, J. L. Hall,* Joint Institute for Laboratory Astrophysics, University
of Colorado and National Bureau of Standards, Boulder, Colorado 80309

   We study state-dependent spin-rotation coupling by analysis of well-
resolved hfs spectra of HF obtained with a frequency-controlled color-center
laser spectrometer. A CH_4-stabilized laser controls a 3.39 µm auxiliary laser
with a frequency-synthesizer phase lock loop. A dual-wavelength transfer in-
terferometer is locked to this auxiliary laser and stabilizes the color-center
laser using rf sideband techniques. The system provides digital frequency
scanning and observed resonance line widths below 20 kHz. HF ground state hfs
coupling constants of Muenter and Klemperer[1] are used while the excited state
hfs constants are adjusted to fit our spectra for R(0), P(2), P(3) and P(4)
lines. Excellent fits are obtained but large changes in C_F (-17%) and C_H (-3%)
are required. We can semiquantitatively account for these changes in terms of
the highly anharmonic vibrational potential and the resulting large changes in
$\langle r_e^{-3} \rangle$ with excitation.[2]

*Staff Member, Quantum Physics Division, National Bureau of Standards.

[1] J. S. Muenter and W. Klemperer, J. Chem. Phys. 52, 6033 (1970).
[2] D. K. Hindermann and C. D. Cornwell, J. Chem. Phys. 48, 4148 (1968).

RA3.   (10:15)

ULTRA SENSITIVE IR LASER ABSORPTION SPECTROSCOPY OF TRANSIENT RADICALS AND IONS

D.J. NESBITT, H. PETEK, P.R. OGILBY, C. GUDEMAN, R.J. SAYKALLY, AND C. BRADLEY MOORE

   In this work, a tunable difference frequency laser system is employed to obtain high qua-
lity, Doppler-limited infrared spectra of transient molecular radicals generated by excimer
laser photolysis, and molecular ions produced in an AC glow discharge.

   The response time of the high resolution, flash-kinetic ir spectrometer is $\leq$ 100 nsec,
with an absorption sensitivity of $\leq$ 0.5% over a 100 cm pathlength, permitting detailed spectro-
scopic, kinetic, and photofragmentation studies of a wide variety of transient radicals. Data
and analysis are presented on the ν_1 and ν_3 CH stretching spectra of singlet methylene over
the region 2600 - 3050 cm^{-1}. Strong interaction between the singlet and ground state triplet
manifold is indicated by significant perturbations in the spectrum, and can be sensitively
observed by magnetic modulation of the triplet coupled states.

   For obtaining molecular ion absorption spectra in an AC glow discharge, velocity modula-
tion techniques are employed. By dual beam subtraction of laser amplitude noise, near shot
noise sensitivity limits of $\leq 10^{-6}$ absorbance/$Hz^{1/2}$ have been achieved. Data is presented
on the ν_1 DN stretching mode in DNN^+; transitions out to J = 20 in both P and R branch are
observed for $(10^00) \leftarrow (00^00)$ and the hot band $(11^10) \leftarrow (01^10)$. Rotational constants for ground
ground and excited states, vibrational frequencies, and ℓ-type doubling constants for the ν_2
excited states are reported. Rotational state distributions appear equilibrated in the liquid
nitrogen cooled discharge and correspond to a 190 K temperature.

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RA4.

(10:50)

OBSERVATIONS OF INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION DYNAMICS IN S_1 AROMATICS

K.W. HOLTZCLAW, C.S. PARMENTER, AND B.M. STONE

The method of chemical timing, that is to say, the restriction of fluorescence lifetimes by addition of an electronic quencher such as O_2, has been used to monitor the time evolution of vibrational structure in S_1-S_0 fluorescence. In both p-difluorobenzene (pDFB) and p-fluorotoluene (pFT), structure from the pumped S_1 vibrational level is observed in fluorescence at short times (10's of psec) after excitation. That structure disappears at longer observation times as intramolecular vibrational redistribution (IVR) destroys the initial vibrational character. Kinetic analysis reveals that the IVR lifetime is near 10 psec for three levels ($\epsilon_{vib} \approx$ 1200-2000 cm^{-1}) in pFT IVR dynamics are characterized for 11 levels ($\epsilon_{vib} \approx$ 1600-3300 cm^{-1}) in pDFB. There is a trend from long IVR lifetimes (500 psec) to short lifetimes (20 psec) as ϵ_{vib} increases. Within this trend, however, there is marked sensitivity of IVR lifetimes to the identity of the initially pumped zero-order level. The addition of a low frequency mode ($\nu_{30}' \approx$ 120 cm^{-1}) to the pumped level identity is particuarly effective in accelerating the IVR rate.

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RA5.

(11:25)

ROVIBRONIC ENERGY SURFACES AND SEMI-CLASSICAL DYNAMICS OF POLYATOMIC MOLECULES*

William G. Harter

Complex rotational fine structure of semi-rigid spherical, symmetric, and asymmetric top molecules can be clearly related to semi-classical trajectories on rotational energy (RE) surfaces.[1] The RE surface pictures provide ways to visualize the possibilities for complex rotational dynamics of polyatomic rotors and to interpret fine and superfine energy level patterns. An analogy can be made between RE surface dynamics and the dynamics on harmonic on or anharmonic vibrational PE surfaces.[2] The concept of a coherent or minimum uncertainty wavepacket state is one key to this analogy.

The RE surface picture can be extended to treat general rovibronic energy levels which involve multiple nested RE surfaces or a multi-valued RVE surface.[3] For this an analogy can be made to the study of vibronic interactions using multi-valued PE surfaces for the Jahn-Teller or Renner effects. Some examples of scalar and tensor Coriolis interactions in ν_3-like spherical top levels with high J provide a clear and detailed picture of how a molecule can move in various extremes of Hund's cases as well as in between these extremes.

From the examples studied so far it appears that complex rovibronic Hamiltonians can have revealing "pictures" made of them. The pictures and semi-classical calculations based on them can elucidate molecular dynamics as well as spectra associated with rotational, vibrational, electronic, and nuclear orbital or spin angular momentum coupling effects.

Pictures of RE and RVE surfaces will be shown in color using 3D stereo projection if time and equipment permit it.

1. W. G. Harter, and C. W. Patterson, J. Chem. Phys. (in press).
2. W. G. Harter, Mario Blanco, and E. J. Heller (manuscript in preparation).
3. W. G. Harter, J. Statistical Physics-Conference Proceedings on Fractal Structure in Physics (in press).
*Research supported in part by NSF grant PHY-8207150.

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RA6.   (11:50)

Calculated electric and magnetic properties for excited states

of molecular hydrogen

J. Rychlewski

Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina   27514

We have carried out a series of calculations of the electric and magnetic properties for excited states of molecular hydrogen using explicitly correlated wavefunctions. Here we report: static and dynamic polarizability for the $b^3\Sigma_u^+$ state, quadrupole moments, components of magnetizability tensors and rotational g-factors for the $b^3\Sigma_u^+$, $a^3\Sigma_g^+$, $B^1\Sigma_u^+$ and $B'^1\Sigma_u^+$ states. The results presented should be accurate to somewhere between 0.1% and 1%. This error estimation is based on the comparison of the theoretical values obtained in a similar way for the ground state of $H_2^{(1,2)}$ with the appropriate experimental data. It will be shown that molecular properties as functions of R (inter-nuclear distance) become more complicated for higher excited states and that they well mirror the internal structure of the molecule.

1.   J. Rychlewski, J. Chem. Phys. **78**, 7252 (1983).

2.   J. Rychlewski and W. T. Raynes, Mol. Phys. **41**, 843 (1980).

RB1.

DIFFERENCE FREQUENCY SPECTROSCOPY OF THE FUNDAMENTAL BAND OF CH(X$^2\Pi$)

K. G. LUBIC AND T. AMANO

Fifty-four transitions of the fundamental band of CH have been measured using an IR tunable difference frequency system. CH was generated in a dc discharge through 1 torr He and a few millitorr of CH$_4$. Zeeman modulation was used to observe low J transitions, while amplitude discharge modulation was necessary at higher J. A combined fit of these data, microwave-optical double resonance and microwave data yielded values for the band origin, the spin-orbit constant, rotational constants, spin-rotation constants, and lambda-doubling constants for both v = 0 and v = 1 as well as magnetic hyperfine constants for v = 0.

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RB2.

HIGH RESOLUTION SPECTRUM OF THE HCl DIMER

N. OHASHI AND A. S. PINE

Rotational structure in the spectrum of the H-Cl stretching bands of the HCl dimer has been fully resolved using a tunable difference-frequency laser. The spectrum of a natural isotopic sample was recorded under thermal equilibrium conditions near the condensation point (T~130 K) of HCl at low pressures (3-4 Torr) and long pathlengths (64-80 m). Rotational assignments have been made for K"=0, 1, and 2 subbands of a perpendicular-type band centered near 2880 cm^{-1} and a parallel-type band near 2857 cm^{-1} sharing a common vibrational ground state. For the ground state of the H^{35}Cl-H^{35}Cl dimer, the K"=0 rotational constant, B= 1944.29(7) MHz, and the K"=1 asymmetry splitting, B-C=19.5(3) MHz, yield a zero-point center-of-mass separation of the two monomer constitutents of 3.797(1) Å. Another difference band for the ^{35}Cl isotope has also been observed as well as a similar set of bands for the mixed H^{35}Cl-H^{37}Cl species. The spectra suggest an extremely rapid tunneling motion between equivalent forms of nearly orthogonally oriented monomer units.

Address: Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C. 20234.

SUB-DOPPLER LASER STARK SPECTRA OF THE ν_3 BAND OF FORMIC ACID

W. H. WEBER AND P. D. MAKER

Stark-tuned Lamb-dip spectra of HCOOH in the 1750-1790 cm^{-1} region were obtained using a CO laser and an intracavity Stark cell. Approximately 40 laser lines from 4 isotopes of CO were used, and the maximum Stark field was 35 kV/cm. Several thousand individual Lamb dips were observed, only a small fraction of which have been assigned. On the basis of data from 30 resonances associated with various P(5), P(2), R(2), Q(1), and Q(2) lines, analyzed using the CO laser frequencies of Guelachvili et al.,[1] we have determined a preliminary value for the a-component of the excited state dipole moment, μ_a = 1.420 ± 0.005 D. Preliminary values for the excited state molecular constants have also been obtained. Analysis of the spectrum is complicated by a perturbation occurring around K=4 in the excited state. Most spectra recorded near the band center show intense zero-field level crossing resonances. These appear in both parallel and perpendicular polarizations, indicating that collisional transfers are very significant.

---

[1] G. Guelachvili, D. de Villeneuve, R. Farrenq, W. Urban, and J. Verges, J. Mol. Spectrosc. 98, 64 (1983).

Address of Weber and Maker: Physics Department, Research Staff, Ford Motor Company, Dearborn, MI 48121.

HIGH RESOLUTION SPECTROSCOPY OF JET-COOLED PROPYNE BY DIRECT INFRARED ABSORPTION

J. WANNA AND D. S. PERRY

Direct absorption of an F-center laser beam in a pulsed free jet is used to measure the acetylenic C - H stretching spectra of propyne and acetylene. The use of a pulsed nozzle offers low temperatures (7 K to 50 K) and low background pressures (10^{-5} Torr range) with modest pumping requirements. Resolution at ~ 100 MHz is better than Doppler limited. The jet-cooled spectra are compared to high resolution FTIR spectra of gas phase samples.

At the lowest temperatures only the K = 0 and K = 1 levels, required by conservation of nuclear spin, are observed. The resolved splitting between these levels provides a value for the difference between ground state and vibrationally excited state rotational constants, A' - A".

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R85.

FAR INFRARED SPECTRA OF H_2O

J. W. C. JOHNS

Spectra of H_2O, $H_2^{18}O$, D_2O and HDO have been recorded in the region from about 15 cm^{-1} to 300 cm^{-1} using a Bomem interferometer at an apodized resolution of about 0.004 cm^{-1}. The accuracy of measurement is, for the most part, better than 4 x 10^{-4} cm^{-1} and the frequencies should therefore be useful for the calibration of high resolution spectrometers until more accurate heterodyne measurements become available. Some of the data have been fitted, together with available microwave data, to Watson's A-reduced hamiltonian.

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R86.

THE ν_6 BAND OF C_3O_2

P. JENSEN AND J. W. C. JOHNS

Spectra of C_3O_2 near 540 cm^{-1} have been recorded with a Bomem interferometer at an apodized resolution of 0.004 cm^{-1}. After deconvolution an effective line width of ~0.0018 cm^{-1} has been attained enabling significant progress to be made in the analysis. In addition to confirming an earlier analysis[1] of the fundamental, many of the levels involving up to 3 quanta of the low lying bending vibration ν_7 have also been identified and analysed. Aspects of the vibrational Renner-Teller effect will be discussed.

[1] L. Halonen, I. M. Mills and J. Kauppinen, Mol. Phys. **43**, 913 (1981).

Address of Jensen: Physikalische-Chemisches Institut, Justus Liebig Universität, Heinrich Buff Ring 58, D-6300 Giessen, West Germany.

Address of Johns: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada, K1A 0R6.

RB7.

HIGH RESOLUTION FOURIER TRANSFORM AND DIODE LASER IR SPECTRA OF THE 13.37 MICRON BAND OF PROPA..E GAS

S. J. DAUNT, D. C. REUTER, D. E. JENNINGS, W. E. BLASS, G. W. HALSEY AND J. W. BRAULT

The IR absorption band of propane centered near 748 cm^{-1} has been studied using tne nign resolution FT instrument at Kitt Peak ($\Delta\nu = 0.005$ cm^{-1}) and a tunable diode laser spectrometer (Doppler limited). This is the first study of propane in which individual vibration-rotation lines have been observed. A complete asymmetric rotor analysis of this C-type band has been undertaken and molecular constants for both ground and upper states will be reported. New ground state microwave data taken by Mark Allen at the Jet Propulsion Laboratory has also been included in our analysis and helped provide high accuracy ground state parameters and energy levels. The results of this work are being used for the interpretation of the propane features observed by Voyager in the IR spectra of the atmosphere of Titan.

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Address of Reuter and Jennings: NASA/Goddard Space Flight Center, Infrared and Radio-Astronomy Branch, Code 693, Greenbelt, MD 20771.

Address of Blass and Halsey: Molecular Spectroscopy Laboratory, Department of Physics & Astronomy, The University of Tennessee, Knoxville, TN 37996-1200.

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RB8.

RAMAN SPECTROSCOPY OF GASES WITH A FOURIER TRANSFORM SPECTROMETER; THE RO-VIB SPECTRUM OF D_2

D. E. JENNINGS, A. WEBER, AND J. W. BRAULT

Raman spectra of gases have been recorded using a Fourier transform spectrometer. An argon-ion laser and multiple-pass Raman cell[1] were set up at the McMath FTS of the National Solar Observatory at Kitt Peak. The FTS was operated in the conventional manner, except that a photomultiplier was used as a detector. The cell was placed both inside and outside the laser cavity, and both laser polarizations were used. Spectra were recorded both with and without Rayleigh blocking filters. The technique was used to produce spectra of pure-rotation and rotation-vibration bands of H_2, D_2, N_2, O_2, C_2H_2, and CO_2. The technique has advantages over the use of conventional grating spectrometers in Raman spectroscopy because of the high throughput, wide spectral coverage, and high calibration accuracy of the FTS. In addition, the large dynamic range of the McMath FTS allows the Rayleigh line to be recorded without filtering.

The spectrum of D_2 was used to measure the frequencies of seven pure-rotation transitions and nine rotation-vibration transitions. Signal-to-noise in the lines was as high as 150 after eight hours of integration, producing accuracies of a few milliwave-numbers. A rotation-vibration analysis of D_2 will be presented.

[1] A. Weber and J. Schlupf, J. Opt. Soc. Am. 62, 428 (1972).

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Address of Weber: National Bureau of Standards, Washington, DC 20234.
Address of Brault: National Solar Observatory, 950 North Cherry Avenue, P.O. Box 26732, Tucson, Arizona 85726.

RB9. (11:16)

0.0025 cm^{-1} RESOLUTION WITH THE KITT PEAK FOURIER TRANSFORM SPECTROMETER

D. E. JENNINGS, R. HUBBARD, and J. W. BRAULT

Molecular spectra have been recorded at 0.0025 cm^{-1} resolution using the 1-meter FTS of the National Solar Observatory located at Kitt Peak. This was accomplished by converting the normal double-input, double-output optical arrangement which single-passes the cat's-eyes to a single-input, single-output arrangement which double-passes the cat's-eyes. The conversion is done in a simple manner by inserting two flat mirrors and a compensator into the infrared beams and by placing the detector at the second input port of the FTS. The HeNe reference interferometer is not affected by the conversion, and the alignment for single-pass operation is not altered, so that conversion to and from the double-pass arrangement requires minimum modification to the instrument. Spectra of several gases have been recorded using the increased resolution of the FTS, and examples of these will be shown.

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RB10 (11:23)

HIGH RESOLUTION INFRARED SPECTROSCOPY OF THE ν_2 and ν_4 SILANE BANDS
J. J. Keady and D. E. Jennings

The Fourier Transform Spectrometer at the McMath complex at Kitt Peak National Observatory has been used to obtain high resolution ($2.5 \cdot 10^{-3}$ cm^{-1}) spectra of the ν_2 and ν_4 bands of silane (SiH_4). A preliminary linelist along with line strengths will be presented. Silane has recently been detected in an astronomical source, and an application of the laboratory data involving the calculation of a synthetic astronomical spectrum will also be presented.

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RB11. (11:35)

MEASUREMENT AND ANALYSIS OF THE ν_2 AND ν_4 INFRARED BANDS OF $^{13}CD_4$

R. S. McDOWELL, M. I. BUCHWALD, M. S. SOREM, A. G. ROBIETTE, C. DEELEY, AND W. A. KREINER

A Fourier-transform infrared spectrum of 91% $^{13}CD_4$ has been recorded between 885 and 1193 cm^{-1} with a resolution of 0.04 cm^{-1}. The frequencies of 600 lines were measured with an accuracy of 0.003 cm^{-1}. Of these, approximately 368 are assigned to allowed transitions in ν_4, 95 to forbidden ν_4 transitions, and 137 to ν_2; maximum upper-state J values are 20 for ν_4 and 19 for ν_2. An interacting-band analysis of the ν_2/ν_4 diad yields spectroscopic constants for these Coriolis-coupled fundamentals and fits the experimental frequencies with a standard deviation of 0.0058 cm^{-1}. A ν_4 P$^+$(12) transition at 943.3812 cm^{-1}, nearly coincident with the 10P(22) emission line of the $^{12}C^{16}O_2$ laser, has been investigated by heterodyne spectroscopy and its detuning -64 MHz, and absorption coefficient determined. Such coincidences may lead to the development of laser analytical techniques for $^{13}CD_4$, which is a useful non-radioactive atmospheric tracer. CD_4 transitions that are close to isotopic CO_2 laser lines have been determined for this purpose and for use in double-resonance experiments.

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RC1.   (9:30)

ELECTRONIC SPECTROSCOPY WITH A BOMEM INTERFEROMETER

W. S. NEIL, D. A. RAMSAY, AND M. VERVLOET

Emission and absorption spectra recorded with a Bomem interferometer in the region 2700 Å to 4 μm will be shown. Examples will include the absorption spectrum of I_2 in the visible region, absorption spectra of O_2 and H_2O using a 33 m absorption tube, and emission spectra of NCO and NH_2 in the visible and near infrared.

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RC2.   (9:42)

EXPERIMENTAL AND THEORETICAL STUDIES OF THE RADIATIVE LIFETIME AND PREDISSOCIATION RATES OF THE $A^2\Delta$ STATE OF PH^+

N. Elander, P. Erman, O. Gustafsson, M. Larsson, M. Rittby and E. Rurarz

The High Frequency Deflection technique has been applied to obtain the radiative lifetime of the $A^2\Delta$ state of PH^+. The predissociation is known to occur for N'>12 for v'=0 and weakly for all N' values of v'=1, and the measured lifetime of the stable rotational levels of v'=0 (1.5±0.2 μs).

In order to deduce the predissociation rates for v'=1 we have also carried out ab-initio CASSCF calculations of the electronic transition moment for the $A^2\Delta-X^2\Pi$ transition. The calculated radiative lifetime of v'=0 was in good agreement with experiment (1.4 μs). For further potential curves were improved by multireference CI calculations and corresponding calculations were carried out for the $^2\Sigma^-$ and $^4\Pi$ states. Weyl's theory for second order differential equations were used to analyse the predissociation mechanism.

The exact mechanism is at this moment not quite clear, although it appears that one state alone can not cause the observed predissociation pattern.

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RC3.   (9:59)

LASER SPECTROSCOPY OF HOLMIUM AND DYSPROSIUM OXIDES

C. LINTON, Y.C. LIU, H. SCHALL, M. DULICK, AND R.W. FIELD

Last year (paper TB3) we reported preliminary results on Holmium Oxide
(HoO) and discussed the energy linkages between the electronic states. In
this paper, we shall present the results of the rotational analysis and the
analysis of the hyperfine structure.

We shall also discuss preliminary results of recent laser induced
fluorescence experiments on Dysprosium Oxide (DyO). Resolved fluorescence
spectra have provided energy linkages between several low lying states. High
resolution excitation spectra show the four abundant Dy isotopes and the
hyperfine structure on the two which have nuclear spin. The results of the
rotational analysis will be presented and discussed in relation to Ligand
Field Theory predictions.

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RC4.   (10:16)

THE $B^2\Sigma \rightarrow A^2\Pi$ SYSTEM OF SiN

S. C. FOSTER

Electronic emission from the SiN radical, produced by the addition of $SiCl_4$ to active
nitrogen, has been known for many years. The spectrum is dominated by a strong $B^2\Sigma \rightarrow X^2\Sigma$ system,
but also contains weaker $D^2\Pi \rightarrow A^2\Pi$, $K^2\Sigma \rightarrow A^2\Pi$ and $L^2\Pi \rightarrow A^2\Pi$ band systems. However, no B → A or
A → X system has been reported and consequently the locations of the A, D, K and L states with
respect to the ground state are unknown.

Results will be presented which demonstrate that the weak 440 nm violet degraded bands
previously assigned to a "$K^2\Sigma$" → $A^2\Pi$ system[1] are part of the $B^2\Sigma \rightarrow A^2\Pi$ system of SiN. The
analysis of these bands shows that $T_e(A^2\Pi)$ = 994.4 cm^{-1}. This very small T_e value places the
A ↔ X system in the mid infrared and explains the lack of observation of this system by
photographic techniques.

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[1] H. Bredohl, I. Dubois, Y. Houbrechts and M. Singh, Canad. J. Phys. 54, 680, 1976.

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RC5.   (10:33)

ROTATIONAL AND VIBRATIONAL CONSTANTS OF SEVERAL LOW-LYING
LEVELS OF NCO FROM 4658Å PUMPED LEF

K.N. WONG*, A.J. KOTLAR, W.R. ANDERSON AND J.A. VANDERHOFF

Previously, we have reported the laser excited fluorescence spectrum of NCO in an atmospheric pressure flame using argon laser excitation.[1] This paper reports a further investigation of the fluorescence from the most interesting of the pump lines, the 4658Å pump line. The fluorescence is obtained, as before, by placing an atmospheric pressure CH_4/N_2O flame in the extended cavity of an Ar^+ ion laser. The resulting fluorescence in the $A^2\Sigma^+ \leftarrow X^2\pi$ system of NCO is dispersed using a 1m monochromator and detected with a vidicon (OMA I). The fluorescence spectrum reveals that the laser pumped rovibronic level, the $(0,0^0,0)$ $F_2 31$, is much more highly populated than any other level. Emissions from this level to the $(0,0^1,0)$, $(1,0^1,0)$, $(0,0^1,1)$ and $(0,1^0,0)$ levels have been observed. Rotational analyses have been performed on the emissions from the pumped rovibronic level to the first three of the above ground state vibrational levels. The frequencies of the two stretching vibrations and the A_v and B_v spin-orbit and rotational constants have been obtained. The results are in excellent agreement with those from a concurrent study.[2] In addition, our previous tentative assignment of the pumping transition as $Q_2 31$ in the $(0,0^0,0) \leftarrow (1,0^1,0)$ band has been confirmed.

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*NAS-NRC POSTDOCTORAL RESEARCH ASSOCIATE

1. W.R. Anderson, J.A. Vanderhoff, A.J. Kotlar, M.A. DeWilde and R.A. Beyer, J. Chem. Phys. 77, 1677 (1982).

2a. R.A. Copeland, D.R. Crosley, and G.P. Smith, submitted to the 20th Symp. (Int.) on Combustion, Ann Arbor, Mich., August 1984.
 b. D.R. Crosley, private communication.

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RC6.

ION LASER EXCITATION OF C_2 AND CN FLUORESCENCE IN A FLAME: ASSIGNMENT OF PUMP TRANSITIONS AND EXCITED STATE ENERGY TRANSFER

K.N. WONG*, J.A. VANDERHOFF, W.R. ANDERSON AND A.J. KOTLAR

Previously, we have reported low resolution fluorescence spectra of C_2 and CN excited by the prism selected lines of Ar^+ and Kr^+ ion lasers in a CH_4/N_2O flame.[1] This paper reports higher resolution studies of these spectra. The C_2 and CN are excited, as before, by placing the flame in the extended cavity of the ion laser. The fluorescence spectra are dispersed in a 1m monochromator and detected with a vidicon (OMA I). Previously, we found that four of the available laser lines pump the C_2 Swan system and eight pump the CN B-X system.[1] This higher resolution study allows assignment of most of the pumping transitions. All of the C_2 pump transitions belong to the Swan system. Curiously, the 5145Å laser line pumps a different transition at high temperature than is observed at low temperature.[2] CN may be pumped by either B-X or B-A transitions, depending upon the laser line selected. Several of the laser lines are found to pump more than one C_2 or CN transition simultaneously, yielding complicated fluorescence spectra. Spectra from those lines which pump a single rotational transition yield information about the relative collisional energy transfer rates of the excited state radicals in the flame. Details of the pump transition assignments and energy transfer rates will be presented.

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*NAS-NRC POSTDOCTORAL RESEARCH ASSOCIATE

1a. J.A. Vanderhoff, R.A. Beyer, A.J. Kotlar and W.R. Anderson, Combust. Flame 49, 197 (1983).
b. J.A. Vanderhoff, R.A. Beyer, A.J. Kotlar and W.R. Anderson, Appl. Opt. 22, 1976 (1983).

2. K. Hakuta, Review of Laser Engineering 2, 568 (1983).

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RC7.   (11:07)

INTRACAVITY Kr^+ LASER EXCITATION OF NH_2
IN AN NH_3/N_2O FLAME

K.N. WONG*, W.R. ANDERSON, J.A. VANDERHOFF, AND A.J. KOTLAR

NH_2 is formed in an atmospheric pressure, premixed NH_3/N_2O flame. Laser fluorescence is excited over the 5400–8000Å region by placing the flame in the extended cavity of a Kr^+ ion laser operating on the 6471Å line. The fluorescence was dispersed using a 1m monochromator and detected with a vidicon (OMA II). The key to the assignment of the pump transition and analysis of the fluorescence spectrum as arising from NH_2 developed from the assumption that the shortest wavelength lines (~5400Å), which are quite strong, probably are due to emission from the laser excited vibronic level in A^2A_1 to the (0,0,0) level in X^2B_1. Analysis of lines in this region yielded a firm assignment to (0,11,0)→(0,0,0) fluorescence. Calculations show that the 6471Å pump line overlaps the $2_{02}-2_{12}$ (and, perhaps slightly, the $3_{03}-3_{13}$) rotational line of the (0,11,0)←(0,2,0) hot band. Relative fluorescence intensities from the various rotational levels in the (0,11,0) excited state support this assignment. The results indicate that rotational energy transfer in the excited state is slow in comparison to vibrational-electronic state relaxation rates in the flame, in agreement with results of Copeland, Crosley and Smith on the (0,7,0) level[1]. The higher signal to noise ratio of the present experiments, however, allows observation of weak fluorescence from rotational levels other than the directly pumped level. Emissions from (0,11,0) to (0,1,0), (1,0,0), (1,1,0) and (0,4,0) also will be discussed.

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*NAS-NRC POSTDOCTORAL RESEARCH ASSOCIATE

1. R.A. Copeland, D.R. Crosley and G.P. Smith, submitted to the 20th Symp. (Int.) on Combustion, Ann Arbor, Mich., Aug 1984.

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RC8.   (11:24)

LASER EXCITED FLUORESCENCE STUDIES OF THE PO RADICAL

W.R. ANDERSON, L.J. DECKER, A.J. KOTLAR AND M.A. DEWILDE

This paper reports preliminary results of laser fluorescence studies of the $A^2\Sigma^+ \leftarrow X^2\pi$ (~2500Å) and $B^2\Sigma^+ \leftarrow X^2\pi$ (~3250Å) transitions of PO. The PO is formed in a microwave discharge through a trace of dimethyl-methylphosphonate seeded into a flow of He or Ar carrier gas. PO fluorescence is excited downstream from the discharge region using a Nd:YAG pumped dye laser. Excitation and fluorescence scans have been performed in both electronic systems. The B-X scans agree well with earlier fluorescence results.[1,2] No previous laser fluorescence studies are available for the A-X system. This system was readily identified by comparison with previous uv absorption studies.[3] The B state lifetime, upon pumping in the Q_1 head of the (0,0) band, was found to be 260ns in excellent agreement with Ref. 1. A (rather crude) measurement of the quenching rate by N_2 is also in reasonable agreement with Ref. 1. Preliminary investigations indicate some dependence of lifetime on rotational level. The A state lifetime was ~11.5ns. This short lifetime is believed to be attributable to an extremely strong A-X transition. Quenching of both A and B states by He and Ar was found to be negligible for up to 10 torr of carrier gas.

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1. M.A.A. Clyne and M.C. Heaven, Chem. Phys. 58, 145 (1981).

2. W.R. Anderson, S.W. Bunte and A.J. Kotlar, Proceedings of the 1982 Chemical Systems Laboratory Scientific Conference on Chemical Defense Research, Special Publication ARCSL-SP-83030, June 1983.

3. K.P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure, Van Nostrand Reinhold Co., New York, 1979 and references therein.

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RC9.   (11:41)

ELECTRONIC ENERGY TRANSFER IN N_2^+

D. H. KATAYAMA

In a previous[1] experiment on the collisional deactivation of electronically excited N_2^+, it was assumed that collision induced electronic energy transfer occurs rapidly between the initial, laser populated $A^2\Pi u(v'=4)$ level and its adjacent ground state, $v''= 8$ level. In the present work, a two laser, optical-optical double resonance technique is used to probe the rotational manifolds of these vibrational levels for the A and X states to show directly and conclusively that rapid electronic energy transfer occurs between these two levels.

Because N_2^+ is homonuclear, its Hamiltonian has no perturbing terms that connect the $A^2\Pi u$ and $X^2\Sigma g^+$ states. Hence, energy transfer between the rotational manifolds of these two different electronic states cannot occur through "gates" of perturbed rotational levels formed in the free molecule. Rotational selection rules deduced from this work will be discussed.

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[1]D. H. Katayama, T.A. Miller and V. E. Bondybey, J. Chem. Phys. 72, 5469 (1980).

_____

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RC10.

PERFORMANCE OF A 300 GROOVES PER MM, 20 CM X 40 CM (8" X 16") BAUSCH AND LOMB PLANE GRATING IN A 10-M CZERNY-TURNER SYSTEM OPERATING IN THE ULTRAVIOLET REGION

C. WELDON MATHEWS, BRAD HARE, P. MISRA, MICHAEL ST. CLAIR, ELMER WILLIAMS JR., AND K. NARAHARI RAO

Reproductions of CO^+ spectra taken with this spectograph, recently modified for photographic recording of ultraviolet spectra, will be compared with spectra obtained earlier on a 3.4-m commercial Ebert spectrograph with a similar but smaller grating. The Czerny-Turner system will be used primarily for flash photolysis studies in the ultraviolet region, where the unusually large grating will provide a relatively fast instrument at resolutions usually limited by Doppler widths or natural line widths.

The emission spectrum of CO^+, $B\ ^2\Sigma^+ - X\ ^2\Sigma^+$, has proved to be a convenient system for making comparisons of intensity and resolution of the two spectrographs, while at the same time providing additional data on the spin doubling constants of these two states. The current data have been analyzed taking full advantage of available microwave data for the ground state, thus permitting comparisons with previous results.

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RE1. (1:00)

A REVIEW OF RECENT INFRARED WORK ON HYDROGEN-BONDED MOLECULES

WALTER J. LAFFERTY, Molecular Spectroscopy Division, National Bureau
of Standards, Washington, D.C., 20234.

RE2. (1:35)

THE H_2S SPECTRUM BETWEEN 2 150 AND 2 950 cm^{-1} : LINE POSITIONS AND INTENSITIES

L. LECHUGA-FOSSAT, J.-M. FLAUD, C. CAMY-PEYRET and J.W.C. JOHNS

Spectra of natural hydrogen sulfide have been recorded between 2 150 and 2 950 cm^{-1} on a
Bomem spectrophotometer with a resolution of 0.010 cm^{-1}. The careful analysis of the $2\nu_2$,
ν_1 and ν_3 bands of the three species $H_2^{32}S$, $H_2^{33}S$ and $H_2^{34}S$ has led to a complete and precise
set of rotational energy levels of the three vibrational interacting states (0 2 0), (1 0 0)
and (0 0 1) for the three isotopes. Then using these data we have been able to determine the
rotational and coupling constants involved in the upper-states Hamiltonian.

About 530 line intensities of $H_2^{32}S$ were measured from which precise transition moments
of the 3 bands under study were derived leading to the determination of the first derivatives
of the dipole moment with respect to the normal coordinates q_1 and q_3 . Besides it is to
be pointed out that the strong intensity anomalies appearing in the ν_3 band are well repro-
duced by the calculation.

Finally the complete spectrum of natural hydrogen sulfide has been computed.

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RE3. (1:52)

FIRST DERIVATIVES OF THE DIPOLE MOMENT OF XY_2 ASYMMETRIC ROTORS: H_2O , NO_2 , H_2S

C. CAMY-PEYRET and J.-M. FLAUD

Since line intensities are proportional to the square of the matrix elements of the
dipole moment operator, the determination of the signs of the dipole moment derivatives
is not a simple problem. We show how it is possible to derive these signs by considering
in the transition moment operators of the fundamental bands the rotational corrections to
the main term in φ_α , the coefficient of which is the purely vibrational transition moment.

The case of the H_2O , NO_2 and H_2S molecules is considered and the first derivatives of
their dipole moment with respect to normal and internal coordinates are given.

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RE4.   (2:09)

CALCULATIONS OF ROVIBRATIONAL SPECTRA OF WATER BY MEANS OF PARTICLES-ON-CONCENTRIC-SPHERES
MODELS

G.A.NATANSON, G.S.EZRA, G.DELGADO-BARRIO, AND R.S.BERRY

Two versions of the adiabatic approach equivalent for states with an equal number of
quanta in local stretching modes have been suggested for calculations of rovibrational levels
of water. If the two modes are not equally populated there exist two possibilities: to treat
symmetric or antisymmetric stretching wave functions as either nondegenerate or quasidegene-
rate. The first possibility leads to the equation for two particles rotating on a sphere. The
second case yields a set of two coupled differential equations. Decoupling the set in the
zeroth order approximation results in the equation for two particles rotating on different
spheres. It has been shown that the particle-on-concentric-spheres (POCS) model allows one to
describe both bending frequencies and rotational structure of the ground and some excited
vibrational states, with accuracy adequate for spectroscopic predictions.

If the radius of the sphere is chosen to coincide with the equilibrium bond length the
potential function turns out to be exactly the same as for the rigid bender model. However
the modification of the kinetic energy suggested here results in a better agreement between
approximate and accurate values of rotational frequencies in the ground and excited bending
states for both H_2O and D_2O. Compared with the rigid bender model, this modification gives
slightly better, approximately the same and slightly worse results for bending frequencies
of H_2O, D_2O and T_2O respectively.

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RE5.   (2:21)

INITIAL STUDIES WITH A BOMEM FTIR SPECTROMETER: THE IR SPECTRUM OF C_2N_2

A. WEBER, W. J. LAFFERTY, AND W. B. OLSON

Initial experiments done and experiences gained with a recently acquired BOMEM DA3.002
Fourier transform spectrometer are described. To facilitate testing of the new instrument
we chose to record and analyze the spectrum of cyanogen which is known from previous studies
at low resolution to have a relatively dense but theoretically well behaved spectrum. The
region of the ν_3 band near 2150 cm^{-1} was recorded with an apodized resolution of 0.004 cm^{-1}
using gas pressures of 1, 5, and 20 torr and a path length of 20 cm. The ν_3 band as well as
several associated hot bands were analyzed. The ν_3 band of OCS near 2062 cm^{-1}, present as
a trace impurity in the C_2N_2 gas, was also observed up to $J \sim 40$ and was used to calibrate the
C_2N_2 spectrum using measured OCS frequencies reported elsewhere [1]. The ν_5 band of C_2N_2 near
233 cm^{-1} was recorded using a gas pressure of 3 torr and path length of 20 cm. Efforts are
underway to record this band with improved signal to noise ratio.

---

[1] G. Guelachvili, Opt. Comm. 30, 361 (1979).

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Standards, Washington, D.C. 20234.

RE6.   (2:39)

MINIMIZATION OF VOLUME AND ASTIGMATISM OF WHITE-TYPE MULTIPLE REFLECTION ABSORPTION CELLS FOR USE WITH CIRCULAR OR SQUARE APERTURES AND IMAGES

W. B. OLSON

The arrangement of Horn and Pimentel[1] for packing four rows of images on the field (front) mirror of a White-type multiple reflection absorption cell, using a row-stepping mirror pair, has been revised and generalized to allow any even number of rows. The images in the field mirror plane exactly fill a rectangular area. Given a desired throughput (etendue) and total path length, it is shown that for minimum volume two conditions must be met. The first is that the rectangle containing the two back mirrors must have the same area as the image space area, and the second is that the two rectangles have the same height-to-width ratio. Neither condition is extremely critical. Closed form expressions have been derived via geometrical optics for image expansion arising from astigmatism, and it is shown that the effect of astigmatism is minimized if the front mirror rectangle is nearly square.

[1] D. Horn and G. C. Pimentel, Appl. Opt. 10, 1892 (1971).

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RE7.   (2:56)

INFRARED INTENSITIES OF SMALL POLYATOMIC MOLECULES CALCULATED FROM CEPA
    DIPOLE MOMENT FUNCTIONS AND ANHARMONIC VIBRATIONAL WAVEFUNCTIONS

P. BOTSCHWINA

Anharmonic vibrational wavefunctions have been calculated from empirically corrected ab initio potentials (SCF or CEPA) by a variational method[1]. Accurate electric dipole moment surfaces are obtained by the coupled electron pair approximation (CEPA) of Meyer[2], the dipole moment being calculated as an energy derivative. Applications concern the IR intensities of stretching vibrations of linear molecules (HCN[3], HCP[3], N_2O, $HCCF$, and HC_3N) and the symmetric bending vibrations of CH_3 and NH_3. Isotope effects are discussed and the accuracy of the familiar "double harmonic" approximation is examined.

[1] P. Botschwina, Chem. Phys. 40, 33(1979); ibid, 68, 41(1982)

[2] W. Meyer, J. Chem. Phys. 58, 1017 (1973); ibid, 64, 2901(1976)

[3] P. Botschwina, Chem. Phys. 81, 73(1983)

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RE8.   (3:25)

ABSORPTIONS OF NH_3, CO_2, H_2O, N_2O, and CH_4 AS INFRARED CALIBRATION STANDARDS:
COMPARISON OF ABSOLUTE ACCURACIES
Linda R. Brown and Robert A. Toth

An absorption spectrum containing the above species has been recorded during an 8 hour period at 0.006 cm^{-1} resolution in the region from 550 cm^{-1} to 5000 cm^{-1} using a Fourier transform spectrometer at Kitt Peak National Observatory. The line positions from this single scan have been compared to values in the literature in order to confirm the absolute accuracies of available standards. The gas sample conditions and references used are as follows:

Species	Path (m)	Pressure (Torr)	Region (μm)	References	Accuracies (10^6 cm^{-1})
NH_3	193	0.001	11.0	1) Poynter et al., Mol. Phys. 51, 393 (1984)	100
CO_2	193	1.03	11.0	2) Freed et al., IEEE QA-16, 1195 (1980)	2
H_2O	10	.01+	6.0	3) Guelachvili, J. Opt. Soc. Am. 73, 137 (1983)	50
N_2O	2.4	3.5	9.0	4) Guelachvili, Canad. J. Phys. 60, 1334 (1982)	50
			2.2	5) Pollock et al. (in preparation)	100
CH_4	2.4	0.03	3.3	6) Knight et al., IEEE IM-29, 257 (1980)	0.1

Detailed comparisons reveal that the laser standards (CO_2, CH_4 and N_2O) and the NH_3 parameters to be consistent within the accuracies of the present data (± 0.0001 cm^{-1}) but that the values of Refs. 3 and 4 are systematically high by 0.0002 to 0.0004 cm^{-1}, values larger than the stated accuracies.

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RE9.   (3:37)

SATURATION LAMB DIP SPECTROSCOPY USING MICROWAVE MODULATION SIDEBANDS ON CO_2 LASER LINES: THE

ν_2 BAND OF AMMONIA

G. MAGERL, W. SCHUPITA, J.M. FRYE, W.A. KREINER and T. OKA

We have measured fifteen vibration-rotation transitions in the ν_2 band of NH_3 to extremely high accuracy ($< \pm 250$ kHz) by means of sub-doppler Lamb dip spectroscopy. In six of these transitions, we have resolved the hyperfine structure due to nuclear quadrupole coupling. As a result, we have been able to determine the vibrational dependence of eqQ in NH_3. The values of eqQ for the 1^+ and 1^- states are $-4442(156)$ and $-4329(375)$, respectively.[3] The former is in excellent agreement with previous work.[1]

We feel that these measurements of NH_3, when combined with the analysis of Urban and co-workers[2,3], will provide a frequency standard of very high precision (10^{-5} cm^{-1}) in the 10 u region.

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[1] M. Juhayoun, C.J. Bordé and J. Bordé, Mol. Phys. 33, 597 (1977)

[2] S. Urban, V. Spirko, D. Papoušek, J. Kauppinen, S.P. Belov, L.I. Gershtein and A.F. Krupnov, J.Mol. Spect., 88, 274 (1981).

[3] S. Urban, D. Papoušek, J. Kauppinen, K. Yamada and G. Winnewisser, J. Mol. Spect., 101, 1 (1983).

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RE10.   (3:54)

THE ν_2 SPECTRUM OF NH_3

R. L. POYNTER, JACK S. MARGOLIS

The spectrum of NH_3 between 720 and 1300 cm^{-1} has been analyzed and 489 lines of the ν_2 band (up to $J=17$) have been assigned. Molecular vibration-rotation con-constants up to 8th order have been determined. The absolute precision of the line positions (as determined from comparison to laser heterodyne measurements made by Sattler et al. and also Hillman et al.) is approximately 50×10^{-6} cm^{-1}. The RMS standard deviation of the fit to the 8th order Hamiltonian is 0.2×10^{-3} cm^{-1}. 21 lines corresponding to $\Delta K = 3$ have been observed. The interactions producing these so-called "forbidden" transitions will be discussed as well as their relative strengths.

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J. J. Hillman, T. Kostiuk, D. Buhl, J. L. Faris, J. C. Novaco, M. J. Mumma, Optics Letters 1, 81 (1977).

Address: Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109.

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USE OF LONG-PATH FOURIER TRANSFORM INFRARED SPECTRA FROM KITT-PEAK IN THE STUDY OF AMMONIA

Š. URBAN, R. D'CUNHA, JON MANHEIM AND K. NARAHARI RAO

Fourier Transform spectra of $^{14}NH_3$ and $^{15}NH_3$ have been obtained with the multiple reflection White type cell (16 m baselength) at Kitt Peak. The advantage of using long path FTS data over a wide spectral range will be discussed by illustrating some of the results recently obtained for ammonia. These include the possibility of identification of forbidden transitions, the extension of assignments in the ν_2 band to higher J quantum numbers and the observation and assignments of many hot bands. These measurements have also made it possible to complete and to correct the assignments of vibration-rotation transitions (up to $J' = 11$-12) to the energy levels $2\nu_2$, ν_4, $\nu_2 + \nu_4$ and $3\nu_2$ which have formed the basis for a new analysis of this complex system of interacting levels. The Hamiltonian matrix including all essential perturbations and the numerical model developed will be discussed.

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SPECTRUM OF THE ν_2 BAND OF $^{15}NH_3$ WITH A PRECISION BETTER THAN 0.0005 CM^{-1}

L. HENRY, A. VALENTIN, R. D'CUNHA, Š. URBAN AND K. NARAHARI RAO

High resolution Fourier Transform spectra of $^{15}NH_3$ have been recorded with a precision better than 0.0005 cm^{-1}, in the ν_2 band region. A simultaneous least squares analysis of these data together with previously published data including recent data on forbidden transitions has been carried out. The $\Delta k = \pm 3n$ interactions have been included in the analysis. The possibility of using these frequencies for calibration purposes in the infrared will be discussed.

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RE13.

THE ANALYSIS OF THE $\nu_1 + \nu_2$ AND $\nu_1 + \nu_2 - \nu_2$ BANDS OF $^{14}NH_3$ AND $^{15}NH_3$

Š. URBAN, P. MISRA, R. D'CUNHA, and K. NARAHARI RAO

The analyses of the $(\nu_1 + \nu_2)$ and $(\nu_1 + \nu_2 - \nu_2)$ bands of ammonia in the Fourier transform spectra, in the region 3100 - 4600 cm^{-1} have been carried out. The assignments of these transitions for $^{15}NH_3$ have been made for the first time. The advantage of simultaneously analysing the combination band and its hot band will be discussed. The data have been used in a least squares fit to obtain a set of constants for the upper state.

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RE14.

ENERGY LEVELS OF AMMONIA

Š. URBAN, R. D'CUNHA, K. NARAHARI RAO AND D. PAPOUŠEK

Precise values for ground state energy levels of $^{14}NH_3$ and $^{15}NH_3$ were obtained from extensive sets of experimental data. Microwave, submillimeter wave pure inversion transitions in the ground and ν_2 states, far IR inversion-rotation transitions in the ground state and vibration-rotation transitions in ν_2 band (measured by two-photon, laser Stark, FTS, and diode laser heterodyne techniques) were simultaneously processed together with all forbidden transitions by the method of least squares. This extensive data set completely describes the energy levels for all possible quantum numbers K, including the spacing of the levels with different K, up to J = 17, for both $^{14}NH_3$ and $^{15}NH_3$. Various approximations of parametrization have been used.

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RF1. (1:00)

THE $\tilde{A}^1A''$ EXCITED ELECTRONIC STATE OF HCN: ISOTOPIC EVIDENCE THAT UNIFIES EXPERIMENT AND THEORY

G. A. BICKEL and K. K. Innes

High resolution vacuum ultraviolet absorption spectra of $D^{13}CN$ and $DC^{15}N$ are photographed, especially for comparison with the so called β-X system, observed previously only for DCN.[1] Isotopic shifts establish the absolute vibrational numbering for this system yielding its assignment to the $\tilde{A}^1A''-\tilde{X}^1\Sigma^+$ transition. The measured bands between 53200 and 65100 cm^{-1} are thereby accommodated by a single electronic transition as predicted by theory.[2] New vibrational constants of the $^1A''$ state are presented for DCN as well as for the two heavier isotopes.

[1] G. Herzberg and K. K. Innes, Can. J. Phys., 35, 842-879 (1957).

[2] G. M. Schwenzer, C. F. Bender and H. F. Schaefer, Chem. Phys. Lett., 36, 179-182 (1975).

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RF2. (1:17)

FLUORESCENCE MEASUREMENTS ON HCP

Kevin K. Lehmann

Spectrally resolved emission from the $\tilde{A}$ excited state of HCP has been observed. The fluorescence displays a long progression in even quanta of the bend and a short progression in the C-P stretch. Forty one vibrational energy levels have been observed, with the highest having 27 quanta in the bending mode, located at 16,912 cm^{-1} above the ground state. The energy levels are very harmonically spaced, even at the highest energy observed. Dr. Stephen Ross is attempting to fit a bending potential to the data, using the semi-rigid bender Hamiltonian, and this will be presented if completed. The result of lifetime measurements of the excited states of HCP will also be presented.

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RF3. (1:34)

INFRA-RED EMISSION SPECTRA OF NH_2

M. VERVLOET

Fourier transform spectra of the emission of NH_2 have been recorded at high resolution using a Bomem spectrometer. In the special range 2600-3500 cm^{-1}, transitions of the vibrational fundamental ν_1 of NH_2 are observed as well as the ν_1 and ν_3 fundamentals of NH_3 and the $\Delta v = 1$ sequence of NH in its $X^3\Sigma^-$ electronic ground state. Only a few weak lines of the 110 - 010 band can be detected and no lines of the fundamental ν_3 have been identified. Between 6000 and 10000 cm^{-1}, the emission arises from the electronic transition $\tilde{A}^2A_1 - \tilde{X}^2B_1$ of NH_2; the lines involve the lowest vibronic states of each K_a value in the upper $\tilde{A}^2A_1$ state and the 020 or 030 vibrational levels in the $\tilde{X}^2B_1$ lower state. From the rotational analyses, improved molecular constants will be presented.

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RF4.

MICROWAVE-OPTICAL DOUBLE RESONANCE OF HNO AND DNO IN THE $\tilde{A}^1A''(000)$ STATE

J. C. PETERSEN, S. SAITO, T. AMANO, AND D. A. RAMSAY

The microwave-optical double resonance technique has been used to observe rotational transitions in the $\tilde{A}^1A''(000)$ state of both HNO and DNO. Twenty-nine and thirty-two rotational lines were observed in HNO and DNO, respectively, in the frequency region from rf to 90 GHz. They were analyzed to give effective rotational and centrifugal distortion constants. Perturbations were found in K-type doubling transitions for several subbands. Microwave transitions between levels in the $^1A''(000)$ state and 'extra' levels were observed in HNO.

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RF5.

LASER-INDUCED FLUORESCENCE MEASUREMENT OF SPIN-ORBIT SPLITTINGS IN EXCITED VIBRATIONAL LEVELS OF NCO $(X^2\Pi_i)^*$

RICHARD A. COPELAND AND DAVID R. CROSLEY

In this study on NCO we use the combination of laser excitation and a CH_4/N_2O atmospheric pressure flame to furnish new high resolution spectroscopic information on a ground state transient molecule in excited vibrational levels. The linear NCO molecule is of interest both spectroscopically, since the $X^2\Pi_i$ state has a Renner-Teller split bending vibration with possible Fermi resonances, and chemically, as an intermediate in several combustion mechanisms.

We have undertaken a detailed investigation of these NCO ground state levels $0\nu_2 0$, $1\nu_2 0$, $2\nu_2 0$, $0\nu_2 1$, and $1\nu_2 1$ where ν_2 varies from 0 to 2 in some cases. Spin-orbit splitting constants A, rotational constants and vibrational band origins are extracted for several previously unobserved vibrational levels. A preliminary fit to band head positions shows that the magnitude of A (in cm^{-1}, with typical 0.3 cm^{-1} error) decreases with ν_1 and increases with ν_3: $A_{000}=-95.5$; $A_{100}=-90.0$; $A_{200}=-71.8$; $A_{001}=-97.3$; $A_{101}=-92.6$. The Renner-Teller splitting also changes with stretching vibrations. Similar variations in the spin-orbit coupling constants are seen in $BO_2(X^2\Pi_g)^1$ and $NCS(A^2\Pi_i)^2$. These molecules possess a strong Fermi interaction which may also contribute to the large spin-orbit splitting variations in the ν_1 levels of the $X^2\Pi_i$ state of NCO.

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[1] R. N. Dixon, D. Field and M. Noble, Chem. Phys. Lett. 50, 1 (1977); K. G. Weyer, R. A. Beaudet, R. Straubinger, and H. Walther, Chem. Phys. 47, 171 (1980).

[2] R. N. Dixon and D. A. Ramsay, Can. J. Phys. 46, 2619 (1968).

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RF6.   (2:20)

SPECTROSCOPY OF Cs_3^+

H. HELM, R. MÖLLER, K. STEPHAN, P. C. COSBY, and D. L. HUESTIS

The electronic structure of Cs_3^+ has been investigated by photodissociation of fast (2-5 keV) Cs_3^+ molecular ions (formed by field ionization from a liquid cesium droplet) using dye lasers and fixed frequency lines from argon and krypton ion lasers covering portions of the wavelength region between 406 and 850 nm.

Both Cs^+ and Cs_2^+ photofragments are detected. The photodissociation cross section, the branching between dissociation pathways, and the kinetic energy released in the dissociation are all found to vary significantly with the excitation wavelength. In the infrared (1.5-2 eV) dissociation into Cs^+ and two ground state Cs atoms is the dominant channel. At higher photon energies the Cs_2^+ pathway becomes important. For both pathways the energy released in the center-of-mass is surprisingly small, varies linearly with the photon energy and drops abruptly when the next threshold for electronic excitation of the neutral fragments is reached. Preliminary analysis suggests a bond energy of Cs_3^+ with respect to dissociation into Cs^+ + Cs + Cs of 1.3 eV.

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RF7.   (2:32)

ASSIGNMENT OF THE $3p^2F_2 - 3s^2A_1$ ELECTRONIC TRANSITION OF ND_4

JAMES K. G. WATSON

The 14820 cm^{-1} Schüler band of ND_4 has been observed in emission[1-3] and absorption[4,5]. The structure of the recent high-resolution absorption spectrum of this band obtained in a flash discharge experiment[5] is shown to be fully accounted for as the 0-0 band of the transition $3p^2F_2 - 3s^2A_1$. The lifetime of the $3s^2A_1$ ground state is consistent with neutralized ion beam experiments[6]. The $3p^2F_2$ upper state shows significant spin-orbit coupling ($G_{3/2} - E_{5/2}$ = 9.155 cm^{-1}) and Jahn-Teller rotational effects[7]. The theory of the structure of the 1-0, 0-1, and 1-1 bands in the degenerate vibrations will also be discussed.

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[1] H. Schüler, A. Michel and A.E. Grün, Z. Naturforsch. 10a, 1 (1955).
[2] G. Herzberg, Faraday Disc. Roy. Soc. Chem. 71, 165 (1981).
[3] K.P. Huber and T.J. Sears, to be published.
[4] E.A. Whittaker, B.J. Sullivan, G.C. Bjorklund, H.R. Wendt and H.E. Hunziker, J. Chem. Phys. 80, 961 (1984).
[5] F. Alberti, K.P. Huber and J.K.G. Watson, to be published.
[6] G.I. Gellene, D.A. Cleary and R.F. Porter, J. Chem. Phys. 77, 3471 (1982).
[7] J.K.G. Watson, J. Mol. Spectrosc. 103, 125 (1984).

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RF8.   (3:10)

CS$_2$ CONTINUUM - LIKE EMISSION

Y. S. Lee and S. J. Silvers

The emission spectrum of gas phase CS$_2$, excited by a nitrogen laser, consists of discrete bands superimposed upon an apparent continuum. The discrete structure is known to be res-onance fluorescence arising from the T ^{1}A$_2$ state. The continuum is not as well understood. This work investigates the origin and nature of the continuum - like emission.

The ratio of continuum to discrete intensities has been measured at different CS$_2$ pressures. A significant amount of the continuum emission is pressure or collision dependent, but the ratio does not extrapolate to zero in the low pressure limit (below 1 mtorr). Part of the emission persists in the absence of collisions.

The continuum extends from below 400 nm to the red detection limit. Lifetimes are observed to depend on the detection wavelength, varying from 4 μsec at 435 nm to 8 μsec at 484 nm.

It appears that a range of levels, populated from initially excited states by inter and intramolecular relaxation processes, give rise to the continuum - like emission. The levels responsible for the red emission region have longer lifetimes than those responsible for the blue region.

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RF9.   (3:22)

HIGH RESOLUTION ABSORPTION CROSS SECTIONS OF OXYGEN IN THE REGION 193-204 nm OF THE SCHUMANN-RUNGE BANDS AND HERZBERG CONTINUUM

A.S.C. Cheung, K. Yoshino, D.E. Freeman and W.H. Parkinson

Cross sections of oxygen at 300 K have been obtained from photoabsorption measurements at various pressures, from 50 to 760 torr, throughout the wavelength region 193-204 nm with a 6.65 m photoelectric scanning spectrometer equipped with a 2400 lines/mm grating and having an instrumental width (FWHM) of 0.0013 nm. The spectral features contributing to absorption in this region are the discrete lines of some Schumann-Runge bands and underlying dissociation continua consisting of the weak Herzberg continuum of O$_2$ and a pressure dependent continuum attributed to the collision complex O$_4$. Analysis of the pressure dependence of the total continuum cross section measured in window regions between discrete lines yields the Herzberg continuum cross section, for which our value is smaller than previous laboratory determinations in this region. Band oscillator strengths f(0,0) = 2.95×10^{-10} and f(1,0) = 3.13×10^{-9} of the (0,0) and (1,0) Schumann-Runge bands have been determined by direct numerical integration of the measured discrete cross section remaining after subtraction of the continua from the total cross section.

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RF10.   (3:39)

HIGH RESOLUTION CROSS SECTION MEASUREMENT OF OZONE IN THE WAVELENGTH REGION 240-350 nm

D.E. Freeman, K. Yoshino, J.R. Esmond and W.H. Parkinson

Relative cross sections of the Hartley-Huggins bands of O_3 at 195 K have been obtained based on Hearn's values at several Hg-lines. Photoabsorption measurements have been carried out with a 6.65 m photoelectric scanning spectrometer equipped with a 2400 line mm^{-1} grating and operated at an instrumental width (FWHM) of 0.003 nm. Fine structures in the cross section in the Huggins band are observed with shallow features of width 0.01-0.02 nm superposed on stronger broad bands. Absolute cross sections at 298 K, 228 K and 195 K have also been measured at 13 different wavelength points including the 5 ultraviolet Hg-line wavelengths used by Hearn.

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RF11.   (3:56)

HIGH RESOLUTION ABSORPTION CROSS SECTION MEASUREMENTS OF SO_2 AT 213 K IN THE WAVELENGTH REGION 172-240 nm

K. Yoshino, D.E. Freeman, J.R. Esmond and W.H. Parkinson

Laboratory measurements at high resolution of absorption cross sections of SO_2 at the temperature 213 K have been performed in the wavelength region 172-240 nm with a 6.65 m scanning spectrometer/spectrograph operated at an instrumental width of 0.002 nm. The cross sections are measured at wavelength intervals of 0.1 cm^{-1} for sharp bands and 0.4 cm^{-1} for diffuse bands. The cross sections of the sharp bands are quite sensitive to the instrumental width and the present results are more accurate than previous measurements made at low resolution.

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RF12.   (4:08)

SPECTROSCOPIC SURVEY OF THE 550nm REGION OF SUPERSONICALLY COOLED NO_2

MENG-CHIH SU AND DAVID L. MONTS

In a further attempt to unravel the visible system of nitrogen dioxide, we have recorded laser excitation spectra of supersonically cooled NO_2 in the 550nm region. This spectral region was chosen for investigation because low resolution absorption spectra clearly show a sudden increase in intensity and in spectral conjestion beginning at about 550nm. We report the results of our search for $^2B_1$ vibronic bands in this region.

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RF13.   (4:25)

MULTI-PHOTON PHOTODISSOCIATION OF XENON DIFLUORIDE

DAYO ALUGBIN AND ALLAN L. SMITH

When xenon difluoride is irradiated with the focussed fourth
harmonic of a Nd-YAG laser, XeF $(B(1/2) - X(1/2))$ and
$D(1/2)-X(1/2)$ emission results. Measurements of fluorescence in-
tensity versus laser intensity show a multiphoton process is in-
volved. Time-resolved XeF emission, dispersed at a resolution of
0.64 nm, was measured at 10 nsec intervals after the photodis-
sociation using a boxcar integrator. XeF is initially produced
primarily in the $D(1/2)$ state, and there is evidence of subsequent
collision-induced transfer to the $B(1/2)$ state. Radiative
lifetimes of states with low vibrational quantum numbers were
determined at several wavelengths within the B-X and D-X tran-
sitions, both for two different xenon difluoride pressures and as
a function of added nitrogen pressure. The vibrational distribu-
tion in the $D(1/2)$ state has been determined under these con-
ditions.

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RF14.   (4:42)

VUV LASER-INDUCED FLUORESCENCE STUDY OF THE PREDISSOCIATION OF HCN ($\tilde{A} \, ^1A''$)

YEN CHU HSU, MARK A. SMITH, AND STEPHEN C. WALLACE

Direct lifetime measurements of the $\tilde{A} \, ^1A''$ state of HCN and its deuterated isotope

have been made using vacuum ultraviolet laser-induced fluorescence techniques. Appreciable

predissociation rates are seen from low rovibronic levels (v_2'=0-3, v_3'=0-1, J'=0-12, K'=0-2)

of the $\tilde{A}$ state. Strong K dependent predissociation effects are seen but there seems to be no

J-dependence. Moreover, excitation of the bending vibration strongly suppresses the prediss-

ociation processes of the $\tilde{A}$ state. The observed lifetime variations imply the presence of at

least two competing predissociation channels in the $\tilde{A}$ state. Possible predissociation

mechanisms will be discussed.

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RG1. (1:0C)

DEVELOPMENT OF A NEW TUNABLE VISIBLE WAVELENGTH NARROW BAND REJECTION FILTER

PERRY L. FLAUGH, STEPHEN E. O'DONNELL, SANFORD A. ASHER

Recently a patent application for a new optical filter was filed with the U. S. Patent Office[1]. As part of a continuation of this investigation we report on this filter and show its applications in spectroscopy. A new tunable optical filter has been developed which rejects a narrow wavelength interval (50 Å) in the near-UV, visible or near-IR spectral region and allows adjacent wavelengths to pass (T > 90%). This filter is useful in optics, spectroscopy, and for laser applications. The active element of the filters is a crystalline colloidal array of polystyrene spheres. The rejected wavelength is Bragg diffracted from this ordered array. The diffracted wavelength depends upon the crystalline lattice parameters, the crystal structure, and the filter orientation. For a particular sphere concentration and scattering from a particular set of lattice planes, tunability can be achieved by altering the angle between the normal to a set of lattice planes in the filter and the incident light beam. Transmission measurements are used to monitor Bragg diffraction and the resulting light rejection in these filters. The utility of this filter for spectroscopic measurements is demonstrated for Raman spectroscopy. Since a major experimental limitation in Raman spectroscopy results from the high background of elastically scattered light, Raman measurements utilize multidispersing monochromators to reject this "Rayleigh" scattered light. Even in the best state-of-the-art instruments a Rayleigh peak occurs centered at the laser frequency which prevents measurements of Raman peaks at very low frequencies. We demonstrate the utility and advantage of this new filter as a prefilter which selectively rejects the laser wavelength. Raman spectra of polypropylene, a highly scattering material with numerous low frequency modes were measured with and without the filter. These low frequency Raman modes are obscured by the Rayleigh tail even using a double monochromator. However, the filter selectively attenuates the elastically scattered light and allows the low frequency peaks to be observed. We will outline other spectroscopic applications.

RG2. (1:17)

SURFACE SELECTION RULES FOR SERS: CALCULATIONS AND APPLICATION TO THE SERS SPECTRUM OF PHTHALAZINE ON Ag

M. MOSKOVITS AND J.S. SUH

The Surface Selection Rules for SERS is illustrated with the spectrum of phthalazine adsorbed on Ag colloid surface. The relative bands intensities of different modes change with excitation frequencies. In SERS spectrum excited with high frequency laser radiation, bands corresponding to A_1, B_1 and B_2 modes are observed. By using low frequency excitation, on the other hand, only bands corresponding to A_1 modes are observed.

A model calculation will be presented to explain these results.

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RG3.

A VAN DER WAALS STATE OF MATRIX-ISOLATED Cr_2

W. LIMM, T. MEJEAN, AND M. MOSKOVITS

A van der Waals state of chromium dimers in an argon matrix has been detected via 458nm irradiation from an Ar^+ laser followed by an apparent intersystem crossing process.

Resonance Raman study of this state with the 568nm line of a Kr^+ laser shows $w_e''=77.8cm^{-1}$ and $w_e''x_e''=0.01cm^{-1}$.

Lifetime of this state is determined to be ~ 0.5 second, indicative of a spin-forbidden process involved in its relaxation.

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RG4.

SURFACE COHERENT RAMAN SCATTERING ON ZnO OPTICAL WAVEGUIDES

W.M. HETHERINGTON, E.W. KOENIG, N.W. VAN WYCK, R.M. FORTENBERRY, G.I. STEGEMAN

The surface coherent Raman scattering (SCRS) effect has been used to obtain Raman spectra of molecules hydrogen-bonded to ZnO surfaces. Two dye laser beams at frequencies ω_1 and ω_2 are coupled into an oriented, polycrystalline ZnO planar waveguide through $SrTiO_3$ prisms. The evanescent fields are mixed through the $\chi^{(3)}$ of the surface species to produce a guided wave at $\omega_3=2\omega_1-\omega_2$ which is subsequently coupled out of the waveguide through a second prism. Using interference effects resulting from particular choices of TE modes for the three fields, signals from submonolayer coverages of surface species can be detected.

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RG5.   (2:03)

ISOLATED CH STRETCHING MODES IN NORMAL ALKANES: CAN ISOTOPIC SUBSTITUTION AFFECT CONFORMER POPULATION?

W.F. MURPHY

Isolated CH stretching modes in normal propane, butane and pentane have been observed in the gas phase Raman spectra of $C_n HD_{2n+1}$ (n=3,4,5)[1]. Both specifically protonated samples and the h_1 "impurity" in perdeuteriated samples were studied. Assignments of the observed bands to the various CH bonds in the different rotational conformers of these molecules is supported by an excellent correlation with variations in CH bond lengths as found in ab initio calculations.[1]

The concern of the present talk is the fact that the relative intensities of bands due to different CH bonds do not follow the expected behavior. Intensity relations had been predicted assuming the intrinsic intensities of each CH stretching mode to be the same, that protons were randomly distributed among chemically equivalent sites, and that relative populations of species differing in carbon chain conformation are the same as known for the fully protonated species.

Arguments will be presented to support the assumption that the intrinsic intensities (for Raman isotropic scattering) should be the same for the various CH bonds. If this is the case, then some chemically equivalent proton sites are apparently preferred over others, causing changes in relative populations from estimates which assume random distribution of protons among such sites. The current status of quantitative explanations of this behavior will be presented.

---

[1] R.G. Snyder, L. Aljibury, H.L. Strauss, H.L. Casal and W.F. Murphy to be published.

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RG6.   (2:35)

RESONANCE RAMAN SPECTRA AND EXCITATION PROFILES OF METAL(II)DITHIZONATES

D. F. MICHALSKA AND A. T. KOWAL

Resonance Raman (RR) spectra of several metal(II)dithizonates [$M(HDz)_2$, M = Ni(II), Pd(II), Pt(II), Cu(II), Hg(II)] have been recorded with a variety of exciting lines. Excitation profiles of the modes enhanced in the RR spectra of Ni(II) complex resolve the broad electronic absorption band into two separate components which are assigned to two CT metal-ligand transitions. On excitation within the $\pi \rightarrow \pi^*$ transition of the azo group the band corresponding to N=N stretching vibration shows the largest enhancement and is located in the region 1365-1318 cm^{-1} in the RR spectra of metal(II)dithizonates. Vibrational assignments are made. Results obtained allow to explain the changes observed in the vibrational spectra of transient photochromic species of Hg(II)dithizonate.

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RG7.   (2:52)

UV RESONANCE RAMAN STUDIES OF AROMATIC AND POLYCYCLIC AROMATIC HYDROCARBONS

SANFORD A. ASHER AND CRAIG R. JOHNSON

In a continuing investigation of the UV resonance Raman spectra of aromatic molecules we have examined the UV resonance Raman excitation profiles of derivatives of benzene and various polycyclic aromatic hydrocarbons (PAH). In contrast to benzene which shows no resonance enhancement with excitation in its 260 nm B_{2u} transition, substituted benzene derivatives such as phenol show significant enhancement and highly structured excitation profiles. UV resonance Raman excitation between 220 and 260 nm of a variety of polycyclic aromatic hydrocarbons which include naphthalene and pyrene result in very intense Raman spectra and rich excitation profiles. The intensities are sufficient to observe PAH species at less than 10^{-6} M concentrations. We have also examined PAH's in complex matrices such as samples of coal liquids. Different excitation wavelengths enhance the Raman spectra of different PAH ring systems. None of the samples we have studied show fluorescence interference; UV Raman spectroscopy excited below 260 nm is less susceptible to fluorescence interference than conventional visible wavelength Raman spectroscopy.

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RG8.   (3:09)

UV RESONANCE RAMAN STUDIES OF AROMATIC AMINO ACIDS

M. LUDWIG, T. SMART, C. J. JOHNSON, S. A. ASHER

UV resonance Raman excitation profiles of phenylalanine, tyrosine, and tryptophan have been measured in the UV spectral region below 300 nm. The excitation profiles of each of these derivatives are characteristic of their resonant electronic transitions. Little enhancement is observed for excitation within the almost symmetry forbidden electronic transition at 260 nm for phenylalanine. Most of the Raman intensity derives from higher energy electronic transitions. Some enhancement is observed in the 275 nm absorption band of tyrosine. In tryptophan the excitation profiles show significant intensity and structure in the 280 nm and the 220 nm absorption bands. The excitation profile maxima of these aromatic amino acids are sufficiently separated that a judicious choice of excitation wavelength permits selective enhancement of each of these aromatic amino acids in an equimolar aqueous mixture. For example, excitation at 225 nm specficially enhances the 757, 877, 1006, 1350, 1550, and 1615 peaks of tryptophan as well as the 824, 1175, 1208,, 1517, 1556, and 1601 bands of tyrosine. Significantly less enhancement is observed for the 1000, 1190, and 1590 cm^{-1} Raman bands of phenylalanine. Thus, the resonance Raman spectra of an equimolar solution of the mixture excited at 225 nm is dominated by the 1006 cm^{-1} and 1350 cm^{-1} peaks of tryptophan and the 1175 cm^{-1} peak of tyrosine. The peaks occurring in the 1500-1700 cm^{-1} region are of comparable intensity and overlap. The excitation profile data detail vibronic interactions within the aromatic amino acid absorption bands. The resonance Raman spectra of the aromatic amino acids will be compared with that of simpler molecules such as benzene, phenol, phenolate and indole. The environmental dependance of the resonance Raman spectra will also be discussed. Little fluorescence interference is observed upon excitation in the 220-270 nm spectral region for tyrosinate, and the resonance Raman spectra of tryptophan can be obtained at wavelengths as long as 280 nm, well within its lowest energy singlet absorption band. These results indicate that UV resonance Raman spectroscopy can be used to probe aromatic amino acids in proteins.

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RG9.   (3:26)

OPTICAL STARK EFFECTS IN THE ROTATIONAL-VIBRATIONAL RAMAN SPECTRUM OF O_2[*]

R. A. Hill, A. Owyoung, and P. Esherick

High-resolution stimulated Raman spectroscopy has been used to observe optical Stark effects in rotational-vibrational transitions in molecular oxygen. Broadening, shifting, and/or splitting of individual Raman lines results from the inhomogeneous optical fields of the intense pump laser. An analysis of the position of a number of normal and satellite lines in both the polarized and depolarized spectra has led to a measurement of a value for the excited state polarizability anisotropy, $\gamma_1 = (1.36 \pm 0.17) \times 10^{-24}$ cm^3, and to a more accurate value for the band origin, $\nu_0 = 1556.385 \pm 0.001$ cm^{-1}. This experimentally determined value of γ_1 represents the first spectroscopic measurement of an excited state polarizability anisotropy.

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RG10.   (3:43)

PRESSURE DEPENDENCE OF THE STIMULATED RAMAN Q-BRANCH SPECTRUM OF D_2 DILUTED IN He, A, AND N_2

G. J. ROSASCO AND W. S. HURST

Foreign gas broadening and shifting of the vibrational Q-branch lines of D_2 has been measured by use of high resolution (10 MHz) CW-stimulated Raman spectroscopy. The foreign gases studied were He, A, and N_2 with D_2 present at 0.1 mole fraction (or less). The measurements were done at 296 ± 0.5 K in the range 0.25 to 3.75 amagat. The (0-1) Q(3) and Q(4) lines were measured with the following results for the shifting and broadening (Γ = HWHM) coefficients:

J	$\partial \nu$ (J)/∂P (10^{-3} cm^{-1}/amagat) [$\pm$0.6]			$\partial \Gamma$ (J)/∂P (10^{-3} cm^{-1}/amagat) [$\pm$0.08]		
	He	N_2	A	He	N_2	A
3	+7.6	-5.9	-9.5	1.67	2.95	3.04
4	+6.4	-5.5	-9.0	1.44	2.55	2.78

The Q-lines of D_2 show large collision (Dicke) narrowing with the minimum line widths approximately 0.4 times the Doppler width. The spectral profiles are shown to be Lorentzian for the condition[1] ql (=momentum transfer x mean free path) ≤ 0.5. Deviations from Lorentzian lineshapes are observed for ql≥ 0.7. For the Lorentzian lineshape region (P>0.25 amagat for A and N_2; P>0.6 amagat for He) the linewidth (HWHM) versus density (amagat) is well described by $\Gamma = D_0/P + (\partial \Gamma / \partial P)P$ with D_0(cm^2/s-amagat) the self-diffusion constant at 1 amagat for D_2 in the mixture and the pressure broadening coefficients given above. The self-diffusion constant for the mixture can be expressed, in the ideal gas limit, in terms of the diffusion of D_2 in pure D_2 and the diffusion of D_2 in the foreign gas. For He and N_2 we find the last mentioned diffusion constant to be in good agreement (3% and 6%, respectively) with literature values of the mutual diffusion coefficient[2], whereas for A our value is 24% lower than the reported value[2].

[1]S.G. Rautian and I.I. Sobelman, Sov. Phys. Uspek. 9, 701 (1967).

[2]B.A. Ivakin and P.E. Suetin, Sov. Phys. Tech. Phys. 8, 748 (1964).

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RG11.

TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY OF DIHALIDE RADICAL ANIONS.

G.N.R. Tripathi, R.H. Schuler and R.W. Fessenden

Resonance enhanced Raman scattering from dihalide radical anions (Cl_2^-, Br_2^-, I_2^-) produced by the pulse radiolysis of aqueous solutions of alkali halides has been investigated by time-resolved Raman technique. Raman excitation was at 359 nm and 370 nm for Cl_2^- and Br_2^- (absorption peaks at 340 and 360 nm respectively) and at 380 nm for I_2^- (absorption peak at 380 nm). The fundamental vibrations and a number of overtones were observed. Anharmonicity in the radical vibrations was observed to be small. Spectral line-widths were found to increase with vibrational quantum number. In the pulse radiolysis of NaCl (0.1 to 1M) mixed with KBr (0.01 to 0.2 M) a weak Raman signal from a transient species, tentatively assigned to $BrCl^-$ has also been observed. These radicals are observed to decay at microsecond times by diffusion controlled second order reactions.

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RG12.

STRUCTURAL INVESTIGATION OF SILICATE SPECIES IN ALKALINE AQUEOUS SOLUTIONS USING RAMAN SPECTROSCOPY

D. C. SHIEH, AND P. K. DUTTA

This study is part of an overall effort to understand the relationship between the silicate species that exist in alkaline medium. Raman spectroscopy provides a convenient and nondestructive method to study these systems without perturbing the equilibrium. The vibrational assignment of the bands to specific structures is the major challenge and will be discussed in the talk.

We find that at large hydroxide ion concentrations (6 M), only the monomeric silicate species $Si(OH)_2O_2^{-2}$ exist in solution. As the hydroxide ion concentration is lowered, the monomeric species $Si(OH)_3O^-$, the dimeric species $Si_2O_7^{-6}$, and the cyclic trimeric and tetrameric species are formed. These species condense into large polymeric rings and at low hydroxide ion concentration (0.05 M), colloidal silica particles are present in solution. The Raman spectra of these colloidal particles are very similar to that of solid vitreous silica. These results and the vibrational assignments of the silica Raman bands based on the solution species will be presented.

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RG13.   (4:34)

TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY OF EXCITED TRIPLET
STATES OF DIPHENYL-POLYENES

G.N.R. Tripathi

The lowest triplet states (T_1) of 1,6-diphenylhexatriene
(DPH) and 1,8 diphenyloctatetraene (DPO) were prepared photo-
chemically by energy transfer from the anthracene triplet state.
The T_1 Raman spectra were generated by excitation in resonance
with the strong $T_1 \rightarrow T_n$ absorptions in the region 420–440 nm
($\varepsilon \sim 10^5$ $M^{-1}cm^{-1}$). The growth and decay of the triplet
population, spectral characteristics and structural implications
will be discussed.

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RG14.   (4:51)

LASER INDUCED FLUORESCENCE INVESTIGATION OF INTRAMOLECULAR HYDROGEN BONDING AND EXCITED STATE
PROTON TRANSFER IN 1,5-DIHYDROXYANTHRAQUINONE

M. H. VAN BENTHEM AND G. D. GILLISPIE

The fluorescence and fluorescence excitation spectra of 1,5-dihydroxyanthraquinone have
been measured at low temperature in Shpol'skii matrices and the fluorescence excitation
spectrum has also been acquired for an argon free jet expansion. There is a dual fluorescence
character to the emission spectra. The short wavelength fluorescence (485–540 nm) is highly
structured and is dominated by progressions in a vibration of frequency ca. 300 cm^{-1}. At wave-
lengths longer than 550 nm there is an approximately ten-fold stronger, relatively unstructured
emission. The short and long wavelength fluorescences have identical excitation spectra. The
first 1000 cm^{-1} of the excitation spectrum is structured and reasonably regular, but is
followed by a region of greater intensity and spectral scrambling. Deuteration of the hydroxy
protons almost totally eliminates the structured short wavelength fluorescence and greatly
weakens the initial part of the excitation spectrum. These observations are interpreted to
indicate the stable form in the excited state is one for which excited state proton transfer
has taken place.

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RH1.

THE ELECTRONIC SPECTRA OF HEXATRIENES

A. SABLJIĆ, J. P. DOERING, AND R. McDIARMID

The optical, two and three photon resonant multiphoton ionization and electron impact spectra of cis and trans-hexatriene were measured and analyzed. To aid in the assignments, two photon RMPI spectrum was also obtained with parallel linearly and con propagating circularly polarized light. Through the combined analyses of the data obtained for both molecules it was possible, for the first time, to absolutely assign the 3p-Rydberg transitions of these polyenes. These assignments and their significance in the general interpretation of the spectra of polyenes will be discussed.

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RH2.

THE $1^1B_u^+ \leftarrow 1^1A_g^-$ ABSORPTION OF JET-COOLED *TRANS,TRANS*-1,3,5,7-OCTATETRAENE

M.F. GRANVILLE, D.G. LEOPOLD, R.D. PENDLEY, and V. VAIDA

The direct absorption spectrum of the first allowed singlet-singlet electronic transition of octatetraene in a supersonic Argon jet will be presented. Cooling results in an order-of-magnitude decrease in the observed width of the origin band at 35553(3) cm^{-1} and a comparable sharpening throughout the spectrum, enabling vibrational frequencies, relative absorption intensities, and bandwidths to be measured with improved accuracy.

In addition to the carbon-carbon stretching modes at 1235(5) and 1645(6) cm^{-1} and the skeletal modes at 197(5), 348(6), and 547(7) cm^{-1} reported for the jet-cooled fluorescence excitation spectrum[1] and the static gas spectrum[2], an in-plane bending mode at 1006(7) cm^{-1} and a carbon-carbon stretching mode at 1201(8) cm^{-1} are observed to be active.

The origin is found to have the largest integrated absorption intensity and the narrowest bandwidth. Vibronic bandwidths increase markedly with excess energy in the $1^1B_u^+$ state, from ~20 cm^{-1} (FWHM) at the origin to ~80 cm^{-1} at 3280 cm^{-1} above the origin.

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[1] L.A. Heimbrook, J.E. Kenny, B.E. Kohler, and G.W. Scott, J. Chem. Phys., **75**, 4338 (1981)

[2] R.M. Gavin, C. Weisman, J.K. McVey, and S.A. Rice, J. Chem. Phys., **68**, 522 (1978).

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RH3.   (1:29)

LEVEL ORDERING IN *CIS-TRANS* ISOMERS OF 2,4,6,8-DECATETRAEN-1-AL AND 2,4,6,8,10-DODECAPENTAEN-1-AL

M.F. GRANVILLE and H. SHEYBANI

The high resolution ($\sim$5 cm^{-1} linewidth) emission and excitation spectra of several *cis-trans* isomers of the conjugated polyene aldehydes 2,4,6,8-decatetraen-1-al and 2,4,6,8,10-dodecapentaen-1-al in alkane matrices at 4.2K will be presented and interpreted in terms of the energy ordering of the $1^1A''$ ($\pi^*\leftarrow n$) and $2^1A'$ ($\pi^*\pi^*\leftarrow\pi\pi$) excited states.

Based on molar extinction coefficients and low resolution spectra in glasses at 77K, other workers[1] have shown that the two states are nearly degenerate in the *all-trans* C_{10} aldehyde, their order being sensitive to the solvent environment, whereas the $2^1A'$ state is lowest in the *all-trans* C_{12} aldehyde. In this paper, we will discuss the dependence of the state ordering on the geometric configuration of the polyene chain. State assignments will be made on the basis of a complete vibronic analysis of the spectra.

[1] P.K. Das and R.S. Becker, J. Phys. Chem., **86**, 921 (1982).

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RH4.   (1:46)

VIBRATIONALLY RESOLVED OPTICAL SPECTROSCOPY OF CIS,TRANS-1,3,5,7-OCTATETRAENE

BRYAN E. KOHLER AND THOMAS A. SPIGLANIN

Vibrationally resolved fluorescence and one photon fluorescence excitation spectra are measured for cis,trans-octatetraene in n-alkane matrices (hexane and octane) at 4.2K. These spectra are surprisingly similar to those measured for trans,trans-octatetraene. There is a weak S_0 to S_1 transition (0-0 at 28645 cm^{-1} in n-hexane) approximately 3400cm^{-1} below the strong S_0 to S_2 transition at 32134 cm^{-1}. The vibrational development of the S_0 to S_1 absorption and fluorescence is that of a symmetry allowed transition unlike the results for the trans,trans isomer. The weak nature of the lowest energy absorption testifies to the importance of multiply excited configurations in the description of S_1. Vibrational modes in S_1 are weakly coupled with S_2 due to the small energy gap; this coupling is energy dependent. Franck-Condon factors for the S_0 to S_2 transition are also estimated. Together with the vibrational development of the S_0 to S_1 transition, these show that neither of the two lowest excited singlet states are significantly distorted with respect to the ground state.

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RH5.   (2:03)

EXCITED SINGLET STATE STRUCTURE AND DYNAMICS OF ISOLATED DIPHENYLPOLYENES

LOU ANN HEIMBROOK, BRYAN E. KOHLER, AND THOMAS A. SPIGLANIN

One photon fluorescence excitation spectra, fluorescence spectra, and single vibrational level decay kinetics have been measured for diphenylbutadiene[1] (DPB) and diphenylhexatriene[2] (DPH) seeded in supersonic helium expansions. In each case a long lived (52.8 nsec for DPB and 90.7 nsec for DPH) doubly excited $^1A_g^*$ state is located well below the lowest singly excited state ($1^1B_u^*$). The $^1A_g^*$ to $1^1B_u^*$ energy gap is 1150 cm^{-1} for DPB and 3400 cm^{-1} for DPH. All of the observed vibrational states have odd inversion symmetry and are coupled to the $1^1B_u^*$ state. Emission produced by excitation of this $1^1B_u^*$ state emanates not from this state but from vibrationally excited levels of the ^1A_g state which are isoenergetic with the initially prepared state. Comparisons of the gas phase data obtained here with that obtained in low temperature matrices provides a clearer picture of the photodynamics and electronic structure of diphenylpolyenes than was previously available.

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[1] Lou Ann Heimbrook, Bryan E. Kohler, and Thomas A. Spiglanin, Proc. Natl. Acad. Sci. USA 80, 4580 (1983)
[2] Bryan E. Kohler and Thomas A. Spiglanin, accepted, J. Chem. Phys. (1984).

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RH6.   (2:20)

FLUORESCENCE FROM THE 1^1B_u STATE OF trans,trans-1,3,5,7-OCTATETRAENE IN A FREE JET

LOU ANN HEIMBROOK, BRYAN E. KOHLER, AND IRVIN J. LEVY

This work reports the fluorescence spectrum and decay dynamics observed when isolated, cold trans, trans-1,3,5,7-octatetraene is excited to the 1^1B_u state. The observed band profiles generated by exciting the zero vibrational level if the 1^1B_u state are well described by the convolution of 12cm^{-1} Lorentzians with the spectrometer response function yield precise information on the ground state vibrational structure. Quantitative consideration of the observed intensities leads to an estimate of the quantum yield for emission.

Measurements of fluorescence intensity verses incident laser power into the non-linear regime allows for an estimate of the absorption cross section (68Å^2) and excited stay decay time (100-300 psec) to be determined.

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RH7.   (2:37)

PHOTOCHEMISTRY OF CIS,CIS OCTATETRAENE IN THE CONDENSED PHASE

BRYAN E. KOHLER AND PRADIP MITRA

cis,cis octatetraene undergoes photoisomerization to cis,trans octatetraene at low temperatures in an n-octane matrix. We have shown that this takes place in the 2^1A_g state and determined the energy barrier for isomerization in this excited state from measurements of the low temperature fluorescence and the temperature dependence of the fluorescence decay rates. The barrier for excited state isomerization will be compared to the much larger barrier that have been implicated for the isomerization on the ground state surface.

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RH8.   (3:10)

LASER FLUORESCENCE STUDY OF CYCLOOCTATRIENE IN A SUPERSONIC EXPANSION

LOU ANN HEIMBROOK AND BRYAN E. KOHLER

Spectroscopic investigations on cyclooctatriene in solution and in the condensed phase at reduced temperatures have shown no observable emission. We report the observation of emission produced by exciting cyclooctatriene seeded in a supersonic helium expansion. The excitation spectrum for this emission has been measured from 34,140 cm^{-1} to 37,500 cm^{-1}. The lowest energy feature is at 34,785 cm^{-1}. Dispersed emission spectra for excitation at a number of vibronic bands in the excitation spectrum have also been measured. Irradiation of cyclooctatriene vapor efficiently produces all trans, octatetraene. Taken together, these measurements make a case for photochemical rearrangement in the isolated molecule.

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RH9.   (3:27)

THE ORDER OF EXCITED STATES IN POLYYNES

BRYAN E. KOHLER, DAVID E. SCHILKE, AND THOMAS A SPIGLANIN

Simple calculations of singlet electronic state energies in linear polyenes predict an A_g ground state with alternating excited states of B_u and A_g symmetry respectively (a review of linear polyenes can be found in reference 1). However, Hudson and Kohler[2] in 1972 showed that the lowest lying excited singlet state in 1,4-diphenyloctatetraene was of A_g symmetry and Schulten and Karplus[3] showed that this result could be predicted theoretically if doubly excited configurations were included in their calculations. This result has also been shown to be general in many polyenes.[3,4]

The question can now be asked if these results carry over to the polyynes. What are the state orderings in polyynes? Does simple theory adequately explain the state ordering of must configuration interaction be included?

In this work the above questions will be addressed with results obtained from 1,4-diphenylbutadiyne and 1,4-dimethylbutadiyne (2,4-hexadiyne).

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[1] B.S. Hudson, B.E. Kohler, and K. Schulten, Excited States Vol. VI Academic Press, New York.
[2] B.S. Hudson and B.E. Kohler, Chem. Phys. Lett. 14, 299 (1972).
[3] K. Schulten and M. Karplus, Chem. Phys. Lett. 14, 305 (1972).
[4] a) B.S. Hudson and B.E. Kohler, J. Chem. Phys. 59, 4985 (1973); b) R.L. Christensen and B.E. Kohler, ibid. 63, 1837 (1975); c) R.L. Christensen and B.E. Kohler, J. Phys. Chem. 80, 2197 (1976).

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RH10.   (3:44)

TWO-PHOTON THERMAL LENSING (TPTL) SPECTROSCOPY OF MONOSUBSTITUTED BENZENES

J.K. RICE, D.S. KLIGER, AND R.W. ANDERSON

TPTL spectroscopy is used to obtain two-photon spectra of the $B_{2u} \leftarrow A_{1g}$ and $B_{1u} \leftarrow A_{1g}$ electronic transitions in liquid phase, neat monosubstituted bnezenes. Circular to linear polarization ratios are also included.

Substituent perturbations are seen to affect the intensity of these transitions. In two-photon spectroscopy the $B_{2u} \leftarrow A_{1g}$ transition is shown to be insensitive to inductive perturbations while the $B_{1u} \leftarrow A_{1g}$ transition is sensitive to inductive perturbations.

The molecules examined are benzene, fluorobenzene, toluene, phenol, and aniline

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RH11.   (4:01)

ODMR STUDIES OF THE PHOSPHORESCENT TRIPLET STATE OF DIHALONAPHTHALENES

A.M. NISHIMURA

The phosphorescent excited states of 1,4-dichloronaphthalene and 1,4-bromochloronaphthalene has been examined by optically detected magnetic resonance (ODMR). Although the crystal structures of these compounds show similarities, the random orientation of the halogens in bromochloronaphthalene causes a large variation in the energy states. The differences in the linewidths of the orientationally disordered crystal are compared to those of the crystal of 1,4-dichloronaphthalene. In addition, dephasing times using pulsed ODMR are reported for the disordered crystal.

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RH12.   (4:13)

RESONANCE RAMAN SPECTRA OF THE GROUND AND LOW-LYING EXCITED ELECTRONIC STATES OF Ru(II) PENTAAMMINE PYRIDINE DERIVATIVES

Y. C. CHUNG, N. LEVENTIS, P. J. WAGNER, AND G. E. LEROI

The electronic spectra of Ru(II) complexes with organic ligands generally exhibit strong absorptions attributable to metal-to-ligand charge transfer (MLCT).[1] MLCT can be viewed as a redox process in which an electronically excited state composed of an oxidized metal ion and an organic radical anion is formed. The energy of the MLCT state in relation to the lowest d-d* ligand-field (LF) transition is quite sensitive to the nature of the organic ligand, including its substituents.[2]

We have investigated both ground and low-lying excited electronic states of a series of ruthenium (II) pentaammine pyridine derivatives, $Ru(NH_3)_5N\langle\bigcirc\rangle\!-\!R$ where R = acetyl, benzoyl, etc. by resonance Raman spectroscopy. The complexes were irradiated with either cw or pulsed laser radiation; in the latter case the same laser pulse was utilized to both prepare and probe the excited electronic state. The ligand Raman spectra in the ground and MLCT states differ significantly. The results will be compared to Raman spectra of the ground state ligand anions, and the excited electronic state assignments will be correlated with the extensive photochemical literature.

[1] P. C. Ford, Coord. Chem. Rev. 5, 75 (1970).
[2] V. A. Durante and P. C. Ford, Inorg. Chem. 18, 588 (1979).

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RH13.   (4:30)

CHARACTERIZATION OF ELECTRONIC STATES OF MIXED-LIGAND Ru(II) ORGANOMETALLIC COMPLEXES BY RESONANCE RAMAN SPECTROSCOPY

Y. C. CHUNG, N. LEVENTIS, P. J. WAGNER, AND G. E. LEROI

The photochemical and photophysical properties of $Ru(bipy)_3^{++}$ [bipy = 2,2'-bipyridine] and other $Ru(d^6)$ complexes have been subjects of intense investigation.[1] These compounds show potential utility in photochemical energy conversion processes and are also of intrinsic interest. Woodruff and coworkers,[2] in an elegant interpretation of the resonance Raman spectra of the ground and lowest metal-to-ligand charge transfer (MLCT) excited electronic states, have demonstrated that the transferred electron in the MLCT state of $Ru(bipy)_3^{++}$ is localized on one bipy ligand rather than being delocalized among all three. That conclusion has been confirmed by other workers.[3]

We have studied a series of $RuL_2M_2^{++}$ complexes, where L = bipy or 1,10-phenanthroline, M = acetylpyridine, benzoylpyridine, etc., by resonance Raman spectroscopy. In these cases two distinct MLCT transitions may arise, and the excited state resonance Raman spectra might serve to characterize which ligands are being "reduced". Raman scattering from the electronic ground states and from model ligand anions have been obtained under resonant cw illumination. Relatively high-power, tuned, pulsed-laser irradiation was used to both form and interrogate the MLCT states. The results will be discussed in terms of the relative MLCT and ligand field (LF) transition energies and the localized electron transfer model proposed for $Ru(bipy)_3^{++}$.

[1] J. V. Caspar and T. J. Meyer, J. Am. Chem. Soc. 105, 5583 (1983), and references cited therein.
[2] P. G. Bradley, N. Kress, B. A. Hornberger, R. F. Dallinger, and W. H. Woodruff, J. Am. Chem. Soc. 103, 7441 (1981).
[3] W. K. Smothers and M. S. Wrighton, J. Am. Chem. Soc. 105, 1067 (1983); S. McClanahan, T. Hayes, and J. Kincaid, ibid., 4486 (1983).

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RH14.   (4:47)

FLUORESCENCE POLARIZATION MEASUREMENTS CONCERNING THE ROLE OF ROTATION IN INTRAMOLECULAR ENERGY TRANSFER

Gilbert M. Nathanson and Gary M. McClelland

Quantum and classical theories indicate that fluorescence polarization from electronically excited molecules is greatly reduced if rotation participates in intramolecular vibrational redistribution. This small polarization results when K is not an approximately good quantum number. We compare the results of model calculations to experiments on p-difluorobenzene.

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FA1.

INFRARED-ZERO-FREQUENCY DOUBLE RESONANCE IN A RESONANT D.C. STARK FIELD*

SANG LEE, A. JACQUES, AND R. H. SCHWENDEMAN

Two years ago,[a] we reported a study of the lineshapes of infrared laser radio frequency double resonance signals in CH_3F that occur when the RF frequency goes to zero for the case when the infrared laser is in near resonance with a vibration-rotation transition. The $^QQ(12,2)$ transition in $^{12}CH_3F$ and the $^QR(4,3)$ transition in $^{13}CH_3F$ were studied. We showed that a theory in which the RF field is treated as a high-frequency Stark effect in the usual two-level system gave only rough qualitative agreement with experiment, and did not predict the changes in lineshape that occurred upon variation of the sample pressure and RF power. We attributed the poor agreement between theory and experiment to some sort of interaction between the many m components of the zero-field transition.

We have now studied the infrared-zero-frequency double-resonance lineshape for the $^QP(2,1)$ transition in CH_3F. A D.C. Stark field applied to the sample cell in addition to the modulated RF field brought the $M = 1\leftarrow0$ transition into resonance with the 9P(22) CO_2 laser. By adjusting the Rabi frequency for the laser interaction and the pressure broadening parameter, very good agreement between the observed and calculated lineshape has been obtained for this single M component. Although the pressure must be kept low because of the high Stark field, sufficient pressure variation has been obtained to allow estimation of the pressure broadening parameter for this transition.

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[a]A. Jacques and R. H. Schwendeman, Symposium on Molecular Spectroscopy, 1982.

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FA2.

MICROWAVE-MICROWAVE FOUR-LEVEL DOUBLE RESONANCE IN NH_3-He AND NH_3-H_2 GAS MIXTURES*

D. B. PETERSON AND R. H. SCHWENDEMAN

Recently, Davis and Green[a] have reported the results of calculations of the four-level double resonance effect that occurs when the amplitude of the microwave absorption for a single transition in NH_3, in an excess of He, is monitored while the microwave power in resonance with a second NH_3 transition is increased to saturation. The recent calculations, which included specific consideration of the effects of the M degeneracy, were compared with the experimental results reported by Oka[b] and by Fabris and Oka.[c] As was the case for previous calculations by Davis and Boggs,[d] the more recent calculations show large discrepancies between observed and calculated values of the four-level effects, especially for the case in which the pump and signal transitions have the same k value.

In order to reduce the possibility that the poor agreement between theory and experiment is the result of some systematic experimental error, we have repeated many of the experimental measurements performed in Oka's laboratory for both NH_3-He and NH_3-H_2 mixtures, and have extended the NH_3-H_2 data. Our measurements, which were performed with apparatus in our laboratory, are in very good agreement with those previously obtained.

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[a]S. L. Davis, and S. Green, J. Chem. Phys. 78, 2170 (1983).
[b]T. Oka, J. Chem. Phys. 49, 3135 (1968).
[c]A. R. Fabris and T. Oka, J. Chem. Phys. 56, 3168 (1972).
[d]S. L. Davis and J. E. Boggs, J. Chem. Phys. 69, 2355 (1978).

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FA3. (8:54)

HIGH RESOLUTION FOURIER TRANSFORM SPECTROSCOPY OF THE ν_3, ν_4, AND ν_6 BANDS OF D_2CO

K. NAKAGAWA, R. H. SCHWENDEMAN, AND J. W. C. JOHNS

The Coriolis-coupled ν_3 (a-type, 1100 cm^{-1}), ν_4 (c-type, 938 cm^{-1}), ν_6 (b-type, 989 cm^{-1}) fundamental vibrations of D_2CO have been recorded with a BOMEM model DA3.002 Fourier transform spectrometer at a resolution of 0.004 cm^{-1} in the 780-1200 cm^{-1} spectral region. A total of 807 ν_3 transitions, 796 ν_4 transitions, and 1546 ν_6 transitions have been assigned. The data from the present analysis have been combined with previous infrared laser Stark, sub-millimeter wave laser, infrared-microwave two-photon, and microwave data to derive a set of vibration-rotation constants for the bands.

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FA4. (9:11)

SATURATION LASER STARK AND LASER MICROWAVE DOUBLE RESONANCE SPECTROSCOPY OF OCS INSIDE A CO_2 LASER CAVITY

J.-G. LAHAYE, W.K. AHMED and A. FAYT

Saturation Stark spectroscopy of Carbonyl Sulfide has been pursued with our Stark cell inside a CO_2 laser cavity. The measurements have been extended to weak hot bands and to high J transitions with quite small Stark shifts. One of them is the R(64) line of the Δ-Σ transition $02^20_c \leftarrow 00^00$, a forbidden transition slightly allowed through the ℓ-type resonance between 02^20 and 02^00. This measurement confirms our assignment of the CW laser emission in OCS observed by B.M. Landsberg [1] : the 9R8 CO_2 laser beam is pumping from (00^00, J=64) to (02^20_c, J=65) and the laser emission reaches the (02^20_c, J=64) level.

A microwave coupler has been adapted to our Stark cell to perform, for the first time, Intracavity Laser Microwave Double Resonance experiments under electrical fields up to 100 kV/cm. Many DR lines are observed in the 10 to 50 GHz range, both in upper and lower vibrational states of OCS Stark transitions. The intracavity sensitivity yields high signal to noise ratios. The width (1 to 2 MHz) of the perfectly symmetrical lines allows frequency measurements within 100 kHz.

Those new data have been added to our previous Stark results and combined with a few MBER measurements from F.H. de Leeuw [2] to improve the determination of the electrical properties of OCS.

[1] B.M. Landsberg, IEEE JQE, QE-16, n° 7, pp. 704-706 (1980).
[2] F.H. de Leeuw, thesis, Nijmegen (1971) and private communication from W.L. Meerts and A. Dymanus.

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FA5.

CO_2 AND CO LASER MICROWAVE DOUBLE RESONANCE SPECTROSCOPY OF OCS. PRECISE MEASUREMENT OF DIPOLE MOMENT AND POLARIZABILITY ANISOTROPY

KEIICHI TANAKA, HAJIME ITO, KENSUKE HARADA, AND TAKEHIKO TANAKA

Laser-microwave double resonance (LMDR) with high electric field was applied to the OCS molecule. Stark Lamb-dip spectra due to the infrared transitions of the $2\nu_2$ $02^00 - 00^00$, 9.6 μm, $2\nu_2$ $20^00 - 00^00$, 5.8 μm, and $\nu_1 + 2\nu_2$ $12^00 - 00^00$, 5.3 μm bands were observed with the CO_2 and CO lasers. The spectra due to the corresponding hot bands. $03^10 - 01^10$, $04^00 - 02^00$, $12^00 - 10^00$, $13^10 - 11^10$, $21^10 - 01^10$, $30^00 - 10^00$; $14^00 - 02^00$. $14^20 - 02^20$, $15^10 - 03^10$, $22^00 - 10^00$; and a few bands of $OC^{34}S$ and $O^{13}CS$ were also identified. Associated with these infrared transitions, more than 90 LMDR signals were detected and assigned to rotational transitions in the eleven vibrational states. 00^00. 10^00, 20^00, 01^10, 02^00, 02^20, 03^10, 04^00, 12^00, 14^20, and 22^00, of the normal species, and in the two vibrational states, 00^00 and 02^00, of both $OC^{34}S$ and $O^{13}CS$.

Dipole moments were determined with accuracies (2.5σ) better than 2×10^{-5} D for all these vibrational states. Polarizability anisotropies were also obtained for some states. The data for the ground, ν_1, and ν_2 vibrational states are, with the 2.5σ uncertainties in parentheses.

	Ground	ν_1	ν_2	
μ	0.715 196 (10)	0.694 413 (5)	0.704 330 (11)	D
$\delta\mu$	-	-0.020 783 (11)	-0.010 866 (15)	D
α	4.67 (11)	4.84 (14)	4.85 (30)	$Å^3$

From the Stark Lamb-dip spectra the origins of various vibrational bands were determined, among which those for the $02^00 - 00^00$ and $03^10 - 01^10$ bands are 31 389 530.4 (25) and 31 566 477.57 (67) MHz. respectively. The dipole moments and band origins obtained in the present study agree well with the available accurate values from molecular beam electric resonance and heterodyne measurement, respectively.

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FA6.

CO_2 LASER-MICROWAVE DOUBLE RESONANCE SPECTROSCOPY AND STARK LAMB-DIP SPECTROSCOPY OF THE ν_5 BAND OF CDF_3

KENSUKE HARADA, MAKOTO HATANAKA, AKIRA INAYOSHI, KEIICHI TANAKA, AND TAKEHIKO TANAKA

The laser-microwave double resonance (LMDR) spectroscopy with intense electric field was applied to the ν_5 band of CDF_3. The dipole moments and polarizability anisotropies in the ground and ν_5 states were determined as follows.

	Ground	ν_5	
μ	1.653 511 (29)	1.658 514 (23)	D
α	-0.77 (32)	-0.58 (48)	$Å^3$

where three times of standard deviations are in parentheses. The dipole moment in the ground state agrees with the result by molecular beam electric resonance. 1.653 498 (11) D. The polarizability anisotropies agree with the sum of the electronic polarizability anisotropy obtained from Kerr effect and the contribution of the vibrational Stark effect. The 2.-1 interaction in the ν_5 state was found to give remarkable perturbations to some rotational levels under the electric field. A new electric field dependent interaction of the 2.-1 type was found to give observable effects. The constants for this interaction as well as for the ordinary 2.-1 interaction were determined. The sign of the l-type doubling constant q_5 was determined by means of double resonance experiment. Other molecular constants were also well determined by LMDR and Stark Lamb-dip spectroscopy.

1 W. L. Meerts and I. Ozier. J. Chem. Phys. 75. 596 - 603 (1981).

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FA7. (10:10)

DIPOLE MOMENT FUNCTION OF OCS

KEIICHI TANAKA, TAKEHIKO TANAKA, AND ISAO SUZUKI

By means of infrared laser-microwave double resonance (LMDR) spectroscopy with intense electric field, we recently measured the precise dipole moments of OCS in the eleven vibrational states, $00^0 0$, $10^0 0$, $20^0 0$, $01^1 0$, $02^0 0$, $02^2 0$, $03^1 0$, $04^0 0$, $12^0 0$, $14^2 0$, and $22^0 0$, of the normal species, and in the two vibrational states, $00^0 0$ and $02^0 0$, of both $OC^{34}S$ and $O^{13}CS$. These dipole moments, which are accurate to $2 \cdot 10^{-5}$ D, were combined with the previous MBER results for $00^0 0$ and $01^1 0$ states of the normal, $OC^{34}S$, $O^{13}CS$, and ^{18}OCS species[1] and the transition moments for various vibrational bands obtained from infrared intensity measurements[2], to determine the dipole moment function of OCS.

Curvilinear coordinates were used to describe the vibrational displacements. The dipole moment was represented in terms of the components parallel and perpendicular to the C O or C-S bond. The dipole moments of various isotopic species may thus be analyzed simultaneously. The vibrational wave functions were calculated by direct diagonalization method with the force field given by Foord et $al.$[3] Signs of some transition moments were inferred in the course of the analysis from the vibrational and isotopic variations of the dipole moment. The dipole moment function thus determined resulted in a satisfactory agreement between the observed and calculated moments. The vibrational changes of dipole moment and the slight isotope dependences were adequately accounted for.

1   J. M. L. J. Reinartz and A. Dymanus, Chem. Phys. Lett. 24, 346-351 (1974).
2   R. T. Kagann, J. Mol. Spectrosc. 94, 192-198 (1982).
3   A. Foord, J. G. Smith, and D. H. Whiffen, Mol. Phys. 29, 1685-1704 (1975).

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FA8. (10:27)

THE TWO-DIMENSIONAL POTENTIAL ENERGY SURFACE FOR THE RING-PUCKERING AND RING-TWISTING OF 1-SILACYCLOPENT-3-ENE-d_0, 1-d_1, AND 1,1-d_2

J. Laane and P. M. Killough

The far-infrared spectra of 1-silacyclopent-3-ene and an isotopic mixture containing both 1-d_1 and 1,1-d_2 species have been recorded and analyzed. In addition to the main ring-puckering series a weak side band series, resulting from molecules in the ring-twisting excited state, was observed for the undeuterated molecule. In the 330-520 cm^{-1} region of the infrared spectrum of the isotopic mixture combination bands of the puckering with the SiHD or SiD_2 rocking were observed. The ring-twisting fundamental was also assigned to the 380.6 cm^{-1} band in this region. Analysis of the data for all three isotopic species results in the following two-dimensional potential energy surface

$$V(cm^{-1}) = 2.08 \times 10^5 x_1^4 - 0.005 \times 10^5 x_1^2 + 54.7 \times 10^5 x_1^2 + 1.70 \times 10^5 x_1^2 x_2^2,$$

where x_1 and x_2 are the ring-puckering and ring-twisting coordinates (in Å) respectively. The potential minimum corresponds to a planar conformation and the positive cross term shows the vibrational interaction to be anti-cooperative.

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FA9. (10:44)

LOW-FREQUENCY VIBRATIONAL SPECTRA AND RING-PUCKERING POTENTIAL ENERGY FUNCTION OF 2-PHOSPHOLENE AND 2-PHOSPHOLENE-1-d$_1$

J. Laane, L. Richardson, J. R. Villarreal, and
M. A. Harthcock

The far-infrared and low-frequency Raman spectra of 2-phospholene, $\overline{CH=CHCH_2CH_2PH}$, and 2-phospholene-1-d$_1$ have been recorded. Four infrared and three Raman ring-puckering transitions were observed for each isotopic species. Kinetic energy expansions, corresponding to reduced masses of 130.42 and 136.72 a.u., were calculated for the two species and these were used to determine the asymmetric potential function for ring-puckering for both molecules: $V(cm^{-1}) = 6.05 \times 10^5 x^4 + 3.24 \times 10^5 x^3 + 10^4 x^2$, where x is the puckering coordinate in $\overset{o}{A}$ units. The minimum at x = 0 corresponds to a puckered (presumably endo) conformation. Inflection points occur in the potential function at x = -0.08 A (where V = 205 cm^{-1}) and x = -0.19 A (where V = 524 cm^{-1}). It is likely that the less-stable planar ring conformation and the less-stable puckered conformation (exo) may be associated with these values.

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FA10. (11:01)

COLLISION-BROADENING PARAMETERS OF ETHANE USING TUNABLE DIODE LASER TECHNIQUES

G. W. HALSEY and W. E. BLASS

Diode laser spectroscopy was used to measure the self and foreign gas collision-broadening parameters of ethane. Foreign gas broadeners include: H_2, He, Ar, N_2, and CH_4. The torsional splitting in ethane makes collision induced widths difficult to measure. The ethane spectrum in the region of interest was simulated with Lorentzian full widths from 0 to 0.005 cm^{-1} in increments of 0.0002 cm^{-1}. The collision induced width was determined by comparing the diode laser spectra and the simulated spectra.

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FA11.   (11:08)

HOT BAND INTENSITIES IN THE ν_9 REGION OF ETHANE USING TUNABLE DIODE LASER SPECTROSCOPY

G. W. HALSEY*, W. E. BLASS, AND D. E. JENNINGS

The ν_9 band of ethane has been studied extensively and line positions and room temperature intensities are well characterized. In this paper we present temperature dependent intensity data on ν_9 as well as the torsional hot band $\nu_9+\nu_4-\nu_4$. This work is concentrated in wavelength regions where ν_9 of ethane is observable using CO_2 laser heterodyne techniques where the hot band intensities are of great interest to astronomers.

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FA12.   (11:25)

THE TORSIONAL GROUND STATE HOT BANDS OF ν_9 OF ETHANE

W. E. BLASS, G. W. HALSEY*, A. A. ATAKAN, D. E. JENNINGS, D. REUTER, AND S. SUSSKIND

Extensive diode laser and Fourier transform spectra of ethane have been recorded in the ν_9 region. The torsional ground state hot band, $\nu_9+\nu_4-\nu_4$, has been assigned for the first time. The parameters B_4, D_4^J, and D_4^{JK}, have been determined from ground state combination differences. The analysis of $\nu_9+\nu_4-\nu_4$ includes the torsion-Coriolis interaction with $4\nu_4$. A partial analysis of the second ν_9 torsional hot band, $\nu_9+2\nu_4-2\nu_4$, will also be presented.

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FA13.   (11:42)

INFRARED DOUBLE-RESONANCE SPECTROSCOPY OF $^{13}CD_4$

L. LAUX, B.R. FOY, D. HARRADINE, AND J.I. STEINFELD

We have measured transitions in the $2\nu_4+\nu_4$ band of $^{13}CD_4$ with an accuracy of better than 0.001 cm^{-1}. The fine structure is fully resolved by the technique of infrared double resonance using a tunable diode laser.[1] Transitions have been observed which originate from the J=11 F_2(2) level in ν_4=1 (ref. 2) (pumped by the 10P(22) CO_2 laser line), and from many neighboring levels which are populated by collisional relaxation. A preliminary set of deduced spectroscopic constants will be presented. The decay of the induced absorptions yields a measurement of the rotational relaxation rate. Our results indicate that the cross-section for rotational relaxation in the excited vibrational state is approximately 50% larger than in the ground state.[3]

[1] M. Dubs, D. Harradine, E. Schweitzer, and J.I. Steinfeld, J. Chem. Phys. 77, 3824 (1982).

[2] Assignment kindly provided by R.S. McDowell and A.G. Robiette, private communication.

[3] L. Laux, B. Foy, D. Harradine, and J.I. Steinfeld, J. Chem. Phys. (in press).

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FA14. (11:59)

A NEW METHOD FOR GENERATING PULSED, TUNABLE, INFRARED RADIATION

J. M. LISY AND D. W. MICHAEL

Optical parametric oscillators using $LiNbO_3$ have been used extensively in the infrared. All previous versions have resonated the high frequency (4000 to 7000 cm^{-1}) component. Such sources have been unable to produce narrow band (<0.1 cm^{-1}) radiation in the 2500 to 4000 cm^{-1} region.

A new cavity design resonating the low frequency (2500 to 4000 cm^{-1}) component has been developed which yields 1 to 3 mj/pulse with a linewidth of 0.6 to 0.8 cm^{-1}. The cavity design allows pumping with a standard Q-switched Nd-YAG laser. The addition of an intracavity etalon should permit high (0.01 to 0.02 cm^{-1}) resolution operation.

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FA15. (12:11)

DOPPLER-FREE TWO-PHOTON SPECTROSCOPY OF SiF_4 WITH A CO_2 WAVEGUIDE LASER

F. HERLEMONT, M. AZIZI and J. LEMAIRE

Doppler-free two photon spectroscopy of the $2\nu_3$ band of SiF_4 has been performed using a CO_2 laser. The technique used relies on the high laser intensity available inside the cavity of a waveguide laser which has already allowed the Doppler-free study of the $2\nu_3$ band of SF_6[1,2]. The detection sensitivity is supplied by laser working near the absorptive bistability threshold. The resolution obtained for these $\lambda = 5\mu m$ spectra is about 100 kHz.

[1] F. HERLEMONT, M. LYSZYK and J. LEMAIRE, Appl. Phys. 24 B, 369-374 (1981).

[2] C.W. PATTERSON, F. HERLEMONT, M. AZIZI and J. LEMAIRE, J. Mol. Spectrosc. to be published.

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FA16.

HIGH RESOLUTION MEASUREMENTS OF INFRARED VIBRATION-ROTATION ABSORPTION LINE STRENGTHS AND LINE FREQUENCIES OF THE ν_2 BENDING MODE OF HOCl(g)

RONALD C. CARLSON, ANTHONY T. YOUNG, AND HAROLD S. JOHNSTON

A tunable diode laser spectrometer was used to determine frequencies and absolute integrated and peak absorption cross sections of 41 transitions of the ν_2 band of HOCl(g), in the region 1266-1270 cm^{-1}. The HOCl was generated by the reaction

$$Cl_2O(g) + H_2O(g) \rightleftharpoons 2HOCl(g).$$
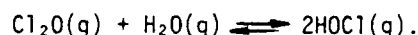
The HOCl concentration was determined by measuring the ultraviolet absorption of the equilibrium mixture from 220 to 270 nm and using available measured ultraviolet cross sections for HOCl and Cl_2O.[1] The absolute integrated and peak line strengths were obtained from nonlinear least squares fits of the measured infrared absorbances to Gaussian and Voigt profiles.

[1]H.-D. Knauth, H. Alberti, and H. Clausen, J. Phys. Chem. 83, 1604 (1979).

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FB1.

OBSERVATION OF THE $a^3\Sigma_g^+ - c^3\Pi_u$, $\Delta v = 1$ SEQUENCE BANDS OF H_2 BY DIFFERENCE FREQUENCY LASER SPECTROSCOPY

TAKAYOSHI AMANO

The $a^3\Sigma_g^+ - c^3\Pi_u$, $\Delta v = 1$ sequence bands of the spectra of H_2 around 4 μm was observed in emission by Dabrowski and Herzberg. We observed the same system in absorption through a modulated d.c. discharge in H_2 (~500 mTorr) with much higher resolution (Doppler limited). The fine structure due to spin-orbit and spin-spin interactions was fully resolved, and these fine structure constants were determined.

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FB2.

H_2 ABSORPTION SPECTRUM IN AN RF DISCHARGE

G. O. BRINK, K. H. KIM, AND A. F. SALIH

The absorption spectrum of electronically excited H_2 is being studied in a microwave discharge using the technique of dye laser intracavity absorption. As of the submission of this abstract, 82 absorption features have been observed between 584 and 601 nm. While most of these correspond to known transitions originating in the c $^3\Pi u$ metastable state of H_2, about 18 do not correspond to transitions assigned by Dieke[1]. The wavelengths of most of these transitions are listed as having been seen in emission, but no assignments are given. We are attempting to assign these transitions. The wavelength range studied is being extended toward both the blue and the red, and additional results will be presented.

The H_2 is excited in a 2500 MHz discharge in a resonant cavity described previously[2]. The pressure in the cavity is about 5 Torr, and the discharge power is 30 watts. No other gases are added to the discharge. The absorption path is about 1 cm long, and, under these conditions, the observed transitions are quite strong. However, signal averaging by means of a computer is used to further improve the signal to noise ratio.

[1] H. M. Crosswhite, "The Hydrogen Molecule Wavelength Tables of Gerhard Heinrich Dieke (Wiley-Interscience, New York, 1972).

[2] G. O. Brink and S. M. Heider, Opt. Lett. 6, 366 (1981).

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(8:59)

FREQUENCY MODULATED VISIBLE LASER ABSORPTION MEASUREMENT OF THE HF 4TH OVERTONE

B. A. WOODY, AND L. LYNDS

With the recent application of frequency modulation techniques to tunable dye laser absorption spectroscopy[1] by Bjorklund, the detection of small concentrations of very weakly absorbing atomic and molecular species has been made possible. We have extended this work to investigate the sensitivity of FM spectroscopy.

We have used a single frequency tunable dye laser, frequency modulated at 250 MHz, to scan the R(4) branch of the HF X $^1\Sigma^+$ ($v = 0 \rightarrow v = 5$) transition ($\Delta E = 18225$ cm^{-1}) in absorption. Line shape profiles were obtained with ±0.0002 cm^{-1} resolution over the pressure range 1-500 torr using only a 26 cm single pass optical configuration. From an analysis of the spectra, the Einstein A coefficient and the dipole-dipole broadening coefficient were obtained. At the present state of development, sensitivity is about four orders of magnitude greater than usual absorption techniques.

This work demonstrates the potential of a technique which can retrieve high resolution lineshape and intensity information from atomic and molecular processes inaccessible to traditional methods. The talk will discuss experimental results and future implications of FM spectroscopy to chemistry and physics.

[1]Gary C. Bjorklund, Optics Letters 5 (1), 15 (1980).

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(9:16)

FOURIER TRANSFORM EMISSION SPECTRUM OF FeO NEAR 1μm

A.W. TAYLOR, A.S-C. CHEUNG, NELSON LEE AND A.J. MERER

The near infrared (4 000 - 14 000 cm^{-1}) spectrum of FeO has been recorded with the 1-meter FT spectrometer at Kitt Peak National Observatory. Like that of the orange system of FeO, the spectrum is very complex and highly perturbed. It consists of two systems: $^5\Phi$-X$^5\Delta$ and $^5\Pi$-X$^5\Delta$. All three states exhibit good case (a) behaviour and have electronic configurations (in single configuration approximation): X$^5\Delta_i$ 3dδ^3 3dπ^2 4sσ^1 and $^5\Phi_i$, $^5\Pi_i$ 3dδ^3 3dπ^2 3dσ^1 4sσ^1 (O 2pπ)^3. The $^5\Phi$ and $^5\Pi$ states lie only about 250 cm^{-1} apart and therefore overlap each other extensively. These states are perturbed by at least three different electronic states, one of which is a Σ state. The most likely candidates for the other perturbing states are $^3\Pi$, $^7\Pi$, $^3\Phi$, and $^7\Phi$, all derived form the same electronic configuration as the $^5\Phi$ and $^5\Pi$ states. We have recently found that the X$^5\Delta$ state is also perturbed, probably by a $^7\Sigma^+$ state (3dδ^2 3dπ^2 3dσ^1 4sσ^1). In total, we have evidence for at least seven electronic states lying below 11 000 cm^{-1} and possibly as many as nine.

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FB5.   (9:33)

THE γ-SYSTEM OF $^{14}N^{34}S$

K.S. CHANDRASEKHAR AND T.K. BALASUBRAMANIAN

Rotational analysis of the 0-0, 0-1 and 0-2 bands of the γ-system (transition:$C^2\Sigma^+ - X^2\Pi_r$) of $^{14}N^{34}S$ has been carried out. The bands, excited in a microwave discharge, had been photographed on a 3.4 m Ebert spectrograph at a reciprocal dispersion of 0.77 Å/mm. From the analysis molecular constants for the C and X states of the isotopic species $^{14}N^{34}S$ have been evaluated. In the fitting procedure the parameters $B^{(1)}_{o_1\text{eff}}$, $B^{(2)}_{o\,\text{eff}}$ and p_o of $X^2\Pi_r$ were constrained to their microwave values[1].

The present analysis confirms the weak predissociation[2] in the $C^2\Sigma^+$ state. Particularly interesting is the presence of a small spin-splitting in the C state with $\gamma_o = +0.0022$ cm^{-1} for $^{14}N^{34}S$ which, however, compares poorly with $\gamma_o = +0.0055$ cm^{-1} for the $^{14}N^{32}S$ species[3]. This large discrepancy might be due to perturbation by a close by $^2\Pi$ valence state.

[1] F.J. Lovas and R.D. Suenram, J.Mol.Spectrosc. 93,416 (1983).

[2] T.K. Balasubramanian, Ph.D. Thesis, University of Bombay (1973).

[3] T.K. Balasubramanian and N.A. Narasimham, J.Mol.Spectrosc. 53,128(1974).

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FB6.   (10:05)

LASER-INDUCED FLUORESCENCE FROM THE $A^2\Delta$, $B^2\Pi$, $C^2\Sigma^+$ AND $G^2\Sigma^-$ STATES OF THE NS RADICAL*

J. B. JEFFRIES, GREGORY P. SMITH, AND DAVID R. CROSLEY

Laser-induced fluorescence has been observed from transitions between $A^2\Delta$, $B^2\Pi$, $C^2\Sigma^+$, and $G^2\Sigma^-$ and the $X^2\Pi$ ground state of the NS molecule. NS was monitored in a flow reactor downstream from a low pressure microwave discharge in SF_6 and N_2. Laser radiation tunable from 228.8-336.0 nm with bandwidth 0.3 cm^{-1} was produced by Raman shifting a frequency doubled dye laser. Rotationally resolved fluorescence excitation spectra of $A^2\Delta$, v'=0-1; $B^2\Pi$, v'=0-12; and $C^2\Sigma^+$, v'=0 been observed. Relative band emission strengths for 12 bands of $A^2\Delta$, 232 bands of $B^2\Pi$ and 6 bands of $C^2\Sigma^+$ have been measured and Franck-Condon overlap factors determined. Preliminary observations indicate collision-induced transitions occur between fine structure levels of $B^2\Pi$. Rapid collisional quenching of $B^2\Pi$, v'=12 and $A^2\Delta$ v'=0 (but not $A^2\Delta$ v'=1 or $B^2\Pi$ v'=1-11) suggests collisional mixing with predissociative levels. Lifetime measurements for $B^2\Pi$ and the observed collisional quenching of $B^2\Pi$, v'=12 are in agreement with the recent results of Matsumi et al.[1]

[1] Y. Matsumi, T. Munakata, and T. Kasuya, J. Phys. Chem. 88, 264 (1984).

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FB7. (10:22)

VIBRATIONAL CONSTANTS DERIVED FROM ROTATIONAL DATA: LaO and YO

Carlos B. Suarez

We report a new set of improved vibrational constants for LaO
and YO and some additional figures for these species. The idea
has been to fill the lack of sufficient and suitable constants
needed to define the potential-well necessary in some calculation
where they are the main limitation, as in Franck-Condon factors
for instance. In order to do this, unreliable head measurements
and little available band origins are ruled out, taking into account
only resolved rotational structure, even if fragmentary. The accura-
cy of the constants is very much increased . Test of the potential-
well is done reobtaining known rotational constants, and for further
consistency numerical calculation of centrifugal distorsion constants
is performed, and comparison shows agreement with experimental data.

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FB8.   (10:39)

THE ATOMIC ORIGIN OF THE ELECTRONIC MOLECULAR STATES FROM THEIR HYPERFINE STRUCTURE

M. BROYER, R. BACIS, S. CHURASSY, J.P. PIQUE

When the internuclear distance in a diatomic molecule is sufficiently large that the exchange interactions are negligible, a good representation of the molecular wavefunctions may be obtained from a separated-atom basis set. In this representation the molecular hyperfine interactions can be predicted from their related atomic values. As examples we have solved completely the calculations for the hyperfine structure for two iodine molecular states, namely the $X(^1\Sigma_g^+)$ and the $E(0_g^+)$ states. The results are in good agreement with experimental determinations. The $E(0_g^+)$ state is a ion-pair state and our predictions when compared with the experimental values clearly descriminate the atomic origin between the different possible asymptotes.

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FB9.   (10:51)

HYPERFINE STRUCTURE IN THE $f(0_g^+)$ IODINE MOLECULAR STATE

Mme A. BOUVIER, R. BACIS, A. BOUVIER, S. CHURASSY, J.P. PERROT

Using a tunable C.W. U.V. laser (<2MHz width) together with a C.W. tunable visible laser (<1MHz width) the hyperfine structure of the second 0_g^+ ion-pair state of I_2, namely the f state, has been investigated for the first time by a C.W. Optical-Optical double resonance technique. Several rovibrational levels of the f state have been studied. The quadrupolar hyperfine constant eQq and the nuclear spin-rotation hyperfine constant C, are consistent with a $^3P_0$ atomic origin of the f state.

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FB10. (11:03)

PRECISE EXPERIMENTAL DETERMINATION OF LONG RANGE PARAMETERS FROM DIATOMIC MOLECULAR SPECTRA : CASE OF I_2 AND LI_2

F. MARTIN, R. BACIS, D. CERNY, S. CHURASSY, J. VERGES

The experimental determination of the usual long range parameters C_5, C_6, C_8, ... of diatomic molecules, is difficult and lacks precision due to strong correlations. Nevertheless their precise determination is particularly useful since it can allow in principle the calculation of the related parameters of the other molecular electronic states with the same configuration. From Fourier Transform high resolution spectra using corrected extrapolations from Le Roy's theory and calculations from RKR potential curves it is possible to obtain determinations which are mutually consistent. Comparison of these results with ab initio calculations have been made in the cases of Li_2 and I_2.

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FB11. (11:15)

STUDY OF EXCITED VIBRATIONAL LEVELS OF THE Na_2 $A^1\Sigma_u^+$ STATE USING MODULATED GAIN SPECTROSCOPY

G.K. CHAWLA, H.J. VEDDER, R.W. FIELD, R. BACIS, and S. CHURASSY

Highly excited vibrational levels of the Na_2 $A^1\Sigma_u^+$ state are observed from v=62 to v=131. The highest level of excitation corresponds to a binding energy of 0.65% of the potential well depth, a classical outer turning point R_+~19.1Å in contrast with R_+(v=0)~3.8Å, and a vibrational frequency of ω~4.6 cm^{-1} in contrast with ω_e~117 cm^{-1}.

These excited levels have poor Franck-Condon factors with thermally populated levels of the ground $X^1\Sigma_g^+$ electronic state. Therefore, modulated gain spectroscopy (MGS) is based upon a triple resonance excitation scheme where Na_2 is used as a gain medium in an optically-pumped-laser (OPL) to transfer thermal population, state-selectively, to high v of the ground state. Transitions from these high v levels of the X-state to high v levels of the A-state have good vibrational overlaps and are excited with a third laser. These absorption resonances are monitored by detecting increases in the saturated gain of the OPL. The three cw lasers are each independently frequency stabilized, resulting in a frequency accuracy of ±0.005 cm^{-1}.

A "long range" analysis of the vibrational and rotational levels determines the Van der Waals coefficients C_3, C_6, and C_8. These reflect the atomic properties of Na ($3^2S_{1/2}$) and Na($3^2P_{3/2}$) states into which the A-state dissociates, such as the transition dipole moments, dipole polarizabilities, and quadrupole polarizabilities. From the C_n-values, we have determined the most accurate value to date of the oscillator strength for the Na ($^2S \rightarrow ^2P$) D lines as well as the dipole polarizability of the Na(^2P) state.

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FB12.   (11:32)

PERTURBATION FACILITATED OPTICAL-OPTICAL DOUBLE RESONANCE STUDIES OF THE Na_2 $a^3\Sigma_u^+$, $b^3\Pi_u$, AND TRIPLET-GERADE RYDBERG STATES

LI LI, S. RICE, AND R.W. FIELD

Various spin-orbit mixed Na_2 $A^1\Sigma_u^+$-$b^3\Pi_u$ levels act as gateways into the triplet manifold. The following triplet-gerade Rydberg states have been characterized by sub-Doppler, OODR fluorescence excitation spectroscopy: $2\ ^3\Pi_g$(33 vibrational levels), $3\ ^3\Pi_g$(17 vibrational levels, absolute vibrational numbering), $1\ ^3\Delta_g$(3 vibrational levels), 4 or 5 $^3\Sigma_g^+$ (1 vibrational level, absolute numbering), and $1\ ^3\Sigma_g^-$ (1 vibrational level). The high vibrational levels of $2\ ^3\Pi_g$ perturb most of the low levels of $3\ ^3\Pi_g$. The mechanism for violet fluorescence from Na_2 vapor is discussed.

The v=0-12 levels of the $a^3\Sigma_u^+$ state are observed in rotationally resolved OODR dispersed $^3\Pi_g$-$a^3\Sigma_u^+$ fluorescence. The correct vibrational numbering of the $b^3\Pi_u$ state is established from short wavelength termination of several $^3\Pi_g$-$b^3\Pi_u$ fluorescence progressions.

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FB13.   (11:49)

ELECTRONIC STRUCTURE OF YbO

S. McDONALD, S. RICE, C. LINTON, M. DULICK, AND R.W. FIELD

A Ligand Field Model has been developed which fits the low energy levels of CeO and PrO. We are now investigating the spectroscopy of YbO to test and refine the theory. Three of the expected ten lowest energy levels [9 from the $4f^{13}(^2F_{7/2})6s$ and 1 from the $4f^{14}$ superconfigurations] have been observed in rotationally analyzed laser excitation spectra, with an additional three levels detected in dispersed fluorescence spectra. Our talk will present an experimental energy level diagram of the low energy states of YbO and use Ligand Field Theory to interpret their relative energy order and hyperfine structure.

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FB14.   (12:06)

MATRIX STUDIES OF LARGE MOLECULE DYNAMICS: EFFECT OF METHYL SUBSTITUTION UPON VIBRATIONAL RELAXATION

V. E. BONDYBEY and P. M. RENTZEPIS

The absorption, laser excitation, and resolved fluorescence spectra of 9-Hydroxyphenalenone and of its methyl-substituted derivatives in solid neon are reported. Analysis of the spectra yields detailed information about the potential function and proton tunnelling both in the S_0 ground state and in the S_1 excited state. Studies of vibrationally unrelaxed fluorescence yield new insights into the rates and mechanisms of vibrational relaxation and energy redistribution. The methyl substitution is found to increase the relaxation rates by at least an order of magnitude. This is interpreted by the presence of a nearly freely rotating CH_3 group and attributed to a V→R type process.

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FB15.   (12:23)

THE DOUBLE-MINIMUM (2) $^1\Sigma_u^+$ STATE OF Na_2

J. VERGES, C. EFFANTIN, J. d'INCAN, D.L. COOPER and R.F. BARROW

The spectroscopic properties of a new double-minimum state, (2) $^1\Sigma_u^+$, of Na_2 have been determined by studies of infra-red fluorescence recorded at high resolution by Fourier transform spectrometry. Some levels (v,J) of the inner well, and a few upper levels (i.e. levels above the potential maximum) are populated by u.v. lines ($\sim$ 350 nm) of krypton-ion and argon-ion lasers. All vibrational levels of the outer well and many upper levels form the lower states in fluorescence from Rydberg states, e.g. (3s,5s) $^1\Sigma_g^+$ populated in two-photon processes (3s,5s) $^1\Sigma_g^+$ ← A $^1\Sigma_u^+$ ← X $^1\Sigma_g^+$ by a ring dye-laser. A potential curve has been derived for (2) $^1\Sigma_u^+$: the two potential minima lie at 28454.6 cm^{-1}, 3.688 Å and 27879.0 cm^{-1}, 6.715 Å respectively, and the energy at the top of the barrier is about 29220 cm^{-1} (energies are given relative to the minimum in X $^1\Sigma_g^+$).

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FB16.   (12:35)

ROTATIONALLY RESOLVED ELECTRONIC SPECTRA FOR URANIUM MONOXIDE

MICHAEL C. HEAVEN, JEAN-PHILIPPE NICOLAI, ERIC K. PARKS, AND STEPHEN J. RILEY

Previous attempts to observe the electronic band systems of uranium monoxide (UO) have been hindered by overlapping spectra which arise from the large number of polymeric oxides that coexist with vapor phase UO. We have overcome these problems by the use of sequential muliphoton ionization of a molecular beam of UO, followed by mass selected ion detection. Several vibronic bands of UO have now been observed by this technique. Spectra were recorded by tuning a pulsed dye laser through the single photon resonances, and ionizing the excited molecules with pulses from a XeCl laser. A time of flight mass spectrometer was used to ensure that only UO^+ ions were detected. Rotationally resolved bands were recorded in the region between 560–600 nm. Many of the bands showed a simple P, Q and R branch structure with $B'=B''$ $=0.333\pm 0.004$ cm^{-1}. Rotational lines with $J'' \leq 3$ were not seen indicating that $\Omega = 4$ for the lower state.

Further analytical and experimental work is in progress on these spectra, and a summary of the results will be presented.

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FB17.   (12:47)

SUB-DOPPLER ZEEMAN SPECTROSCOPY OF CeO

H. SCHALL, J. GRAY, M. DULICK, C. LINTON AND R.W. FIELD

Sub-doppler Zeeman experiments have been done on the [16.5]2-$X_1$2 0-0 band and the [16.5]4-$X_2$3 0-0 band of CeO using a 1.2 kGauss magnet. Excitation spectra for the first lines of these transitions have been recorded at various magnetic fields and splittings have been measured. The g values obtained from these experiments will be reported and a comparison will be made to g values calculated using eigenvectors obtained from a fit of the energy levels of CeO to a crystal field hamiltonian.

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FB18.

EMISSION SPECTRUM OF TeH

N.G. DONGRE, B.P. ASTHANA & C.M. PATHAK

Several new bands have been observed in the region 280 - 225 nm in a Hollow Cathode discharge tube using TeO_2 and a trace of water vapor. These have been assigned to an electronic transition $B'^2\Sigma^+ - X^2\Pi_i$ in the diatomic species TeH. The observed bands fit very nicely into the Deslandres Scheme for a Diatomic Molecule and the derived molecular constants reproduce the measured frequencies well within $\pm$ 2 cm^{-1}, the estimated precision in the measurement. The open structure of the bands and relatively higher values of the Ground State vibrational frequency ω_e = 2661.1 cm^{-1} and anharmonicity constant $\omega_e x_e$ = 36.8 cm^{-1} strongly suggest that the emitterr of the observed band system is TeH. The vibrational constants derived from the analysis are as follows :

Electronic State	$\mathcal{D}_e$	ω_e	$\omega_e x_e$	$\omega_e y_e$
$B'^2\Sigma^+$	41514	2313.4	88.0	4.42
$X^2\Pi_{1/2}$	2120	2661.1	36.8	1.17
$X^2\Pi_{3/2}$	0			

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FB19.

OBSERVATION AND ANALYSIS OF THE $2^1\Sigma_g^+$ STATE OF $^7Li_2$ and $^6Li_2$

R. BACIS, B. BARAKAT, S. CHURASSY, C. LINTON, S. MCDONALD, F. MARTIN AND J. VERGES

A transition in the 4700 - 7100 cm^{-1} region, from the previously unobserved $2^1\Sigma_g^+$ state of Li_2 to the $A^1\Sigma_u^+$ state has been observed in the Fourier Transform Infrared Spectrum of the Laser Induced Fluorescence excited by several lines of the argon ion laser. High resolution data have been obtained for seventeen vibrational levels of the $2^1\Sigma_g^+$ state of $^7Li_2$ and twelve levels of $^6Li_2$, thus establishing the vibrational numbering. Results of the rotational and vibrational analysis will be presented and discussed in relation to recent theoretical predictions.[1]

[1]D.D. Konowalow and J.L. Fish, Chem. Phys. **84**, 463 (1984).

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FC1.   (8:30)

HYDROCARBON-WATER INTERACTIONS: ROTATIONAL SPECTRA AND STRUCTURES OF
ETHYLENE-WATER AND ACETYLENE-WATER COMPLEXES

K. I. Peterson and W. Klemperer

The rotational spectra of ethylene-water and acetylene-water complexes
were observed using the molecular beam electric resonance technique. The
following spectroscopic constants were obtained.

	$C_2H_4-H_2O$	$C_2H_4-D_2O$
B+C (MHz)	7274.734(24)	6929.516(34)
B-C (MHz)	371.102(12)	329.452(121)
A-(B+C)/2 (MHz)	22221(5)	21780(53)
μ_a (Debye)	1.0940(9)	1.0944(60)

	$C_2H_2-H_2O$	$C_2H_2-D_2O$	$C_2D_2-H_2O$	$C_2D_2-D_2O$
B+C (MHz)	5546.480(23)	5111.978(16)	5248.238(40)	4839.981(148)
B-C (MHz)	23.834(4)	36.928(8)	21.178(2)	32.913(44)
μ_a (Debye)	2.0116(5)	2.0851(5)	2.0161(42)	2.0899(42)

For ethylene-water, the rotational constants and low dipole moment are
consistent with a structure in which the water is hydrogen bonded to the double
bond of the ethylene. The center of mass separation of the two molecules is
calculated to be 3.41 Å for $C_2H_4-H_2O$.

The acetylene-water complex is effectively planar with the acetylenic hydro-
gen pointed toward the water oxygen. The molecular center of mass separation
in $C_2H_2-H_2O$ is 3.96 Å which gives a hydrogen bond length of 2.23 Å. The possi-
bility of the presence of a low barrier at the planar configuration will be
discussed.

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FC2.   (8:47)

SPECTROSCOPIC CONSTANTS OF AN ATOM-LINEAR MOLECULE COMPLEX WITH A DOUBLE-MINIMUM POTENTIAL

F. J. LIN AND W. KLEMPERER

A variational multiple perturbation method has been developed for the determination of the rotational constant and centrifugal distortion constant of an atom-linear molecule system with a double-minimum potential, given parameters for its potential energy surface. Within the Hamiltonian H,

$$H = - \frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2 (J-j)^2}{2\mu \, R^2} + b_0 j^2 + V(R,\theta),$$

the potential energy $V(R,\theta)$ is written

$$V(R,\theta) = V_1(R,\theta) + V_2(R,\theta)$$

where each $V_i(R,\theta)$ has a single minimum. The eigenfunctions ϕ_1 and ϕ_2, corresponding to the solution of the zeroth-order problem with $V(R,\theta)$ replaced by V_1 and V_2, respectively, comprise the terms in the variational zeroth-order wavefunction ϕ_o, i.e.,

$$\phi_o = a_1 \phi_1 + a_2 \phi_2.$$

Multiple perturbation theory is then carried out to fourth order to determine the spectroscopic constants.

This model is then used to treat ArHCN to test the possibility that ArHCN may have a double-minimum potential.

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FC3.   (9:04)

ROTATIONAL SPECTROSCOPY AND STRUCTURE OF SEVERAL NH_3 COMPLEXES

G. T. Fraser, D. D. Nelson Jr., K. R. Leopold, and W. Klemperer

The radiofrequency and microwave spectrum of NH_3-CO_2 has been measured using the molecular beam electric resonance technique. The spectrum is characteristic of an asymmetric top in which the NH_3 subunit exhibits effectively free internal rotation. The spectroscopic constants obtained for the ground internal rotor state are presented below.

$(B+C)/2$ (MHz)	3756.178(3)	δ_K (MHz)	0.20(2)
$(B-C)/2$ (MHz)	597.4(2)	δ_J (MHz)	0.007(1)
$A-(B+C)/2$ (MHz)	8035(8)	eQq_{aa} (MHz)	-3.175(4)
Δ_J (MHz)	0.0240(4)	eQq_{bb} (MHz)	1.557(9)
Δ_{JK} (MHz)	0.23(5)	eQq_{cc} (MHz)	1.617(11)
		μ (D)	1.7684(14)

The $N-CO_2$ framework of the complex has C_{2v} symmetry with an N-C weak bond length of 2.9875(4) Å. The average bending angle of the NH_3 subunit is 22.71(5)° with a difference in amplitude of 1.0(4)° between the in plane and out of plane excursions. $(B+C)/2$ for the first excited state ($|m|=1$) is 3753.008(2) MHz and the quadrupole coupling constant $eQq_{aa}(|m|=1)= -3.176(9)$ MHz is identical with that measured for the ground internal rotor state.

The rotational spectrum of the similar complex NH_3-N_2O has also been obtained. The spectrum is complicated by the quadrupolar hyperfine and internal rotation and we are attempting to obtain the structure and three-fold barrier height for this system.

While studying various NH_3 complexes an intense and complicated spectrum was observed for $ArNH_3$. The spectral complexity and observed frequencies demonstrate that this complex is not a symmetrical top.

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FC4. (9:26)

DIPOLE MOMENTS OF CALCIUM MONOHALIDES FROM MOLECULAR BEAM LASER-MICROWAVE

DOUBLE RESONANCE SPECTROSCOPY

W.E. ERNST, S. KINDT and T. TÖRRING

Highly precise ground-state dipole moments of CaCl and CaBr were measured by
using the molecular-beam laser-microwave double-resonance method. Microwave
transitions were observed with linewidths of about 20 kHz. With an electric
field applied Stark shifts of several hyperfine components were recorded. The
determination of the dipole moment from measured line shifts required
diagonalization of the complete energy matrix. Rotational constants were
taken from Möller et al.[1] and spin rotation and hfs constants from Childs et
al.[2],[3]. The fit yielded the following results (statistical error in
parentheses):

$$CaCl \quad X^2\Sigma^+ \quad v=0 \quad \mu=4.265(1)D$$
$$v=1 \quad \mu=4.281(1)D$$
$$CaBr \quad X^2\Sigma^+ \quad v=0 \quad \mu=4.364(3)D$$

An additional systematic uncertainty of 0.02 D arises from the limited
accuracy in determining the distance between the Stark plates but this does
not affect the relative differences of the values. It will be shown that the
Rittner ionic model fails in the calculation of these dipole moments. A
modified model is proposed which takes into account explicitly the large
charge shifts in the metal ions arising from the polarization.

[1] K. Möller, H.-U. Schütze-Pahlmann, J. Hoeft, and T. Törring, Chem.Phys.68,
399 (1982).
[2] W.J. Childs, D.R. Cok, and L.S. Goodman, J.Chem.Phys. 76, 3993 (1981).
[3] W.J. Childs, D.R. Cok, and L.S. Goodman, J.Mol.Spectrosc. 95, 153 (1982).

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FC5. (9:43)

THE STARK-HYPERFINE SPECTRUM OF HYDROGEN FLUORIDE, V=1

S. M. BASS, R. L. DeLEON, AND J. S. MUENTER

The J=1,M=0 to J=1,M=1 radio frequency spectrum was observed in the v=1 excited vibrational
state of HF using MBER spectroscopy. The excited state was populated using a Burleigh color
center IR laser to excite the beam between the source and first quadrupole field. The results
include: $\mu=1.8737$ D, $C_F=361.2$ KHz, $C_H=-69.3$ KHz, direct spin-spin=27.5 KHz, indirect spin-spin=
0.42 KHz.

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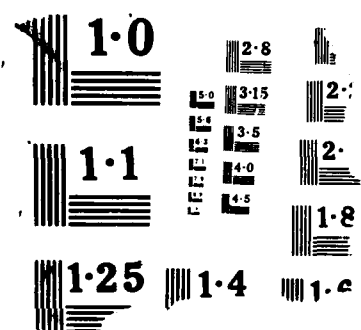
FC6. (10:00)

RADIO FREQUENCY TRANSITIONS IN ACETYLENE-D_2

R. L. DeLEON AND <u>J. S. MUENTER</u>

The ν_5-ν_4 difference band of the vibrational spectrum of deuterated acetylene, DCCD, passes through the microwave and radio frequency portion of the spectrum.[1] The P(16) transition for both the c and d series have been observed by MBER spectroscopy. These transitions consist of strong $\Delta F=1$ components located essentially at the vibrational transition frequency, and weaker $\Delta F=0$ components split by hyperfine interactions. For the c series line, preliminary analysis yields a center frequency of 365.344 MHz, eQq(J=16)=207 KHz, eQq(J=15)= 206 KHz, C(J=16)=C(J=15)=0.4 KHz. The center frequency for the d transition occurs at 3222.44 MHz.

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[1]W. J. Lafferty, R. D. Suenram, and D. R. Johnson, J. Mol. Spec. <u>64</u>, 147-156 (1977).

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FC7. (10:30)

C_2^{*} CHEMILUMINESCENCE FROM OXIDATION OF GAS PHASE CARBON SPECIES BY MOLECULAR OXYGEN

<u>BRIAN G. WICKE</u>

Pulsed laser vaporization of thin carbon films has been used to produce gas phase carbon species under well controlled experimental conditions. Using this technique, we have observed chemiluminescence from the oxidation of these species by molecular oxygen. The carbon beam is shown by mass spectrometry to contain the following species (in order of their relative abundance):

$$C_3 > C > C_2 \gg C_4 \simeq C_5 .$$
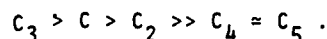
Spectroscopic analysis of the chemiluminescence produced in the reaction of these gas phase species with molecular oxygen is used to identify the reaction product as chemiexcited diatomic carbon, C_2^{*}. The pressure dependence of the chemiluminescence and spectroscopic analysis are consistent with the following reaction

$$C_3 + O_2 \rightarrow C_2^{*} + CO_2 .$$
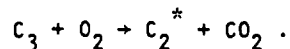
Preliminary experiments under single collision molecular beam conditions confirm that this single reaction step does occur.

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FC8.

Infrared Predissociation Spectra of Water Dimer in a Supersonic Molecular Beam

R. H. Page, J. G. Frey, Y.-T. Lee and Y.-R. Shen

The infrared absorbtion spectrum of the hydrogen-bonded water dimer, $(H_2O)_2$, formed in a supersonic expansion, was recorded in the region of the OH stretch by monitoring the predissociation resulting from the absorption of the radiation. The conditions were such that there was minimal contribution to the observed spectrum from higher water polymers. The observed features show considerable structure, with widths that appear to be limited by the optical resolution of 2 cm^{-1}. A combination band of the OH stretch with the water bend and an overtone of the bending vibration were also observed.

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Address of Frey and Lee: MMRD Lawrence Berkeley Laboratory, University of California and Department of Chemistry, University of California, Berkeley, CA 94720

FC9.

TWO-PHOTON SPECTROSCOPY OF SURFACE SPECIES

N.E. VAN WYCK, E.W. KOENIG AND W.M. HETHERINGTON

Resonant second harmonic generation and fluorescence-detected two-photon absorption in an optical waveguide geometry provide a means of obtaining the two-photon spectrum of interfacial species. If two isotropic media are in contact, then the second harmonic signal is generated only at the interface and, hence, is interface or surface-specific. Spectra of molecules adsorbed onto SiO_2 and ZnO surfaces from gas and liquid phases have been obtained by detecting the second harmonic frequency in resonance with the electronic transitions. The evanescent field of a dye laser beam propagating through a planar waveguide can be used for two-photon excitation spectroscopy of species on the waveguide surface. Spectra of molecules hydrogen-bonded to SiO_2 and ZnO surfaces have been observed.

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FC10.

ROTATIONAL ANALYSIS OF THE $^2A''-^2A''$ ELECTRONIC TRANSITION OF THE SUPERSONICLY COOLED VINOXY RADICAL, CH_2CHO

L. DI MAURO, M. HEAVEN, TERRY A. MILLER

The vinoxy free radical, CH_2CHO, has been produced in situ in a supersonic free jet expansion by ArF laser photolysis of ethyl vinyl ether. Collisions in the jet cool the radical to a rotational temperature of ~10°K. At such temperatures, laser induced fluorescence spectra of the nearly prolate symmetric top vinoxy are quite simple and easily assigned. Both parallel and perpendicular bands have been observed. A detailed analysis yields rotational constants, spin splitting constants, and vibrational frequencies (from band origins) for both the ground and excited states. The implications of these measurements for the geometric and electronic structure of the radical will be discussed.

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FC11. (11:33)

LASER SPECTROSCOPY OF SrOH and CaOH

C. Brazier, S. Kinsey-Nielsen and P. Bernath

The $A^2\Pi - X^2\Sigma^+$ transitions of CaOH and SrOH and the $B^2\Sigma^+ - X^2\Sigma^+$ transition of CaOH were rotationally analyzed by Doppler-limited laser excitation spectroscopy with narrow-band fluorescence detection.

The major constants are (in cm^{-1}, one σ uncertanties):

	To	Bo	Do	γ_0	p_0	Ao
		CaOH				
$B^2\Sigma^+$	18022.268(1)	0.339409(10)	$3.707(100) \times 10^{-7}$	-0.043615(46)	–	–
$A^2\Pi$	15998.128(1)	0.341428(8)	$3.919(27) \times 10^{-7}$	–	-0.043615(46)	66.795(1)
$X^2\Sigma^+$	0.0	0.334354(8)	$3.869(24) \times 10^{-7}$	0.00111	–	–
		SrOH				
$A^2\Pi$	14674.338(1)	0.253889(3)	$2.176(4) \times 10^{-7}$	–	-0.143186(36)	263.515(1)
$X^2\Sigma^+$	0.0	0.249209(3)	$2.182(3) \times 10^{-7}$	0.002433(5)	–	–

The CaOH and SrOH spectra have many similarities to those of the isolectronic CaF and SrF molecules.

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FC12. (11:50)

OBSERVATION OF CALCIUM AND STRONTIUM MONOFORMATES AND RELATED RADICALS

C. Brazier, S. Kinsey-Nielsen and P. Bernath

The reaction of Ca (or Sr) with formic acid (or acetic acid) in a Broida oven[1] produces free radicals of the type $M\overset{O}{\underset{O}{>}}C-R$ (M=Ca,Sr; R=H,CH_3). Additional species are produced by the reactions of alkaline earth metals with acetone and acetaldehyde. Comparison with alkaline earth monohalides, monohydroxides and monomethoxides will be made. Preliminary experiments and assignments will be described.

[1] J. B. West, R. S. Bradford, J. D. Eversole and C. R. Jones, Rev. Sci. Instrum., 46, 164(1975).

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FC13.   (12:07)

VIBRATIONAL PREDISSOCIATION SPECTROSCOPY OF BINARY COMPLEXES INVOLVING BENZENE

A. ALI, M. A. HADWIGER AND J. M. LISY

The vibrational predissociation spectra of $(C_6H_6)_2$, (C_6H_6)-Ar and C_6H_6-Xe
have been measured in the 3000 to 3100 cm^{-1} region using a $LiNbO_3$ optical
parametric oscillator (OPO) and a molecular beam apparatus equipped with a
mass-spectrometer detection system.

The OPO linewidth of 0.6 cm^{-1} is sufficiently narrow to resolve two
components in each $(C_6H_6)_2$ vibrational band. The Ar and Xe complexes have
only one component. The data indicate each component can be assigned to one
of the benzene molecules in the dimer complex. The structural implications of
these results will be discussed.

The predissociation linewidths of the $(C_6H_6)_2$ components, Ar-C_6H_6 and
Xe-C_6H_6 are ~2.0 cm^{-1}. The rotational band contours will be discussed along
with upper state lifetimes.

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FC14.   (12:24)

EXPERIMENTAL AND THEORETICAL STUDIES OF HF DIMER

D. W. MICHAEL, C. E. DYKSTRA AND J. M. LISY

The vibrational predissociation spectrum of HF dimer at low (8 cm^{-1})
resolution,[1] indicated the vibrational frequency of the hydrogen-bonded HF
was approximately 3720 cm^{-1}. In the high (1 MHz) gas-cell absorption spectrum[2]
of $(HF)_2$, a band centered at 3868.079 cm^{-1} was determined to be due to the
hydrogen-bonded HF.

We have reinvestigated the 3720 cm^{-1} at higher (0.7 cm^{-1}) resolution and
have confirmed that it is due to HF dimer.

To resolve the two disparate results, an ab initio potential energy surface
for HF dimer has been determined using a triple-zeta + polarization basis set,
including configuration interaction at the approximate double substituted coupled
cluster (ACCD) level. The results from the potential surface and experiments
will be discussed.

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[1] J. M. Lisy, A. Tramer, M. F. Vernon and Y. T. Lee, J. Chem. Phys. 75, 4733
(1981).

[2] A. S. Pine and W. F. Lafferty, J. Chem. Phys. 78, 2154 (1983).

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STIMULATED EMISSION DUE TO K₂ PHOTODISSOCIATION AND K₂ - K
COLLISSIONS TRANSFER BY TWO-PHOTON PUMPING IN POTASSIUM VAPOR

Z.G.Wang, L.J.Qin, Y.Q.Lin and I.S.Cheng

This paper reports our new results about the generation of stimulated
emission located at 3.14 and 3.16μm by two-photon pumping within suptising
wide wavelength region. It is interesting to find those emission corresponding
to the transition of 5p-3d of K were obtained from a heat pipe oven throughout
the scanning output from 6250 to 6950 Å of a pulse dye laser pumped by a
nitrogen laser. Moreover, at the long wavelength end of the above mentioned
scanning region, even appeared sharp peaks. Fig.1 shows the dependence of re-
lative lasing energy on the pumping wavelength.

We judged that the wide peak in Fig.1 was the stimulated emission follow-
ing the photodissocition of K_2 pumped by two-photon, and the sharp peaks were
that of K which were excited by the resonant collisions energy transfer
between K in the ground state and K_2 in an excited state closely below the
dissociationenergy of a high- lying grade state. Since the energy difference
from the bottom of $X'\Sigma_g^+$ of K_2 to this excited level, which is possible to
dissociate into two seperated atoms of 4s and 5p, is about $E = 28920$ cm⁻¹, the
two-photon energy at the most parts of the scanning region is beyond E. There-
fore, the 5p lever of K is possible to be populated, and the stimulated
emission of 5p-3d is obtained as shown in Fig.2. However, at the long wave-
length end, the two-photon energy
is slightly smaller than E. So K_2
excited from the lowest vibra-
tional level of $X'\Sigma_g^+$ state may co-
llide with K and resonantly trans-
fer the excited energy to it. Thus
the 6p level of K is possible to
be populated and the sharp peaks
were observed. The mechanism was
demonstrated by the effects of the
experimental temprature and pressure
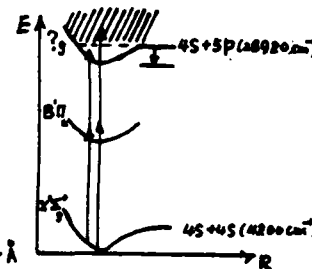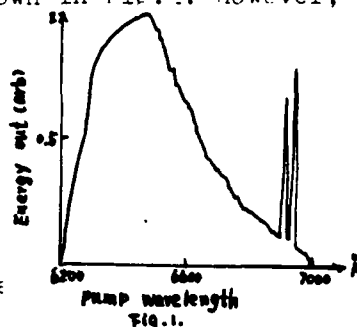
Address of authors: Department of
Physics, East China Normal University, Shanghai,People's Republic of China

Fig.1.   Fig.2.

LASER INDUCED FLUORESCENCE SPECTRA OF THE Br_2He VAN DER WAALS COMPLEX

LAMBERTUS VAN DE BURGT, JEAN-PHILIPPE NICOLAI, AND MICHAEL C. HEAVEN

The Br_2He van der Waals complex has been observed in a free jet expansion.
The complex was detected by laser excitation of the bands associated with the
$Br_2(B-X)$ system. High resolution (0.05 cm⁻¹) spectra have been recorded for the
11-0 to 38-0 bands. On average the band origins for the complex are about 4.2 cm⁻¹
blue shifted with respect to the uncomplexed Br_2 bands. The rotational structure
has been resolved for several bands, and the analysis is found to be consistent with
a rigid 'T' shaped geometry. The distance from the Br_2 band center to the He atom
is 3.8A and 3.5A for the excited and ground states respectively.

Vibrational predissociation of the Br_2-He bond has been observed via homogeneous
broadening of the rotational lines. Predissociation rates, derived from the lineshape
data, showed a strong dependence on the Br_2 vibrational excitation. Rates varied from
10^{10}s⁻¹ for v'=11, up to 5×10^{11}s⁻¹ for v'=38. The data can be adequately described by
a simple 'energy gap' model for the predissociation probability.

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FD1.   (8:30)

MAGNETIC FIELD EFFECTS ON THE HIGH-RESOLUTION

LASER-INDUCED FLUORESCENCE SPECTRA OF THE

MOLECULAR EIGENSTATES OF PYRAZINE AND PYRIMIDINE [1]

J. KOMMANDEUR, W. A. MAJEWSKI, W. L. MEERTS AND D. W. PRATT

Pyrazine (1,4-diazabenzene), when expanded in a seeded and skimmed super-sonic jet of argon and crossed with a 200 kHz wide laser beam resonant with the $^1B_{3u} \leftarrow {}^1A_g$ electronic transition in the near UV, exhibits a laser-induced fluorescence spectrum which consists of many irregularly spaced rovibronic lines lying under each P- and R-branch transition.[2] This structure is believed to have its origin in the coupling between a single zero-order singlet level and several nearly isoenergetic levels of a zero-order triplet state. Proof that this is indeed the case has now been provided by studies of the magnetic field dependence of the spectrum, at low fields between 0-100 G, for several different J' values. The $J'=0$ spectrum exhibits Doppler-broadened lines of width ~ 10 MHz, whereas $J' \neq 0$ spectra show significantly broader lines. An interpretation of these differences in terms of the composition of the molecular eigenstates (ME's), or the "selection rules for intersystem crossing", will be given, and the connection between these spectra and the decay properties of coherently prepared ME's[3] will be established. Similar results for pyrimidine (1,3-diazabenzene), which exhibits qualitatively different behavior in both the frequency and time domains, will be presented.

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[2]B. J. van der Meer, et al., Chem Phys. Letters 92, 565 (1982).

[3]Y. Matsumoto, et al., J. Chem. Phys., in press.

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FD2.   (8.47)

IS PYRIMIDINE AN INTERMEDIATE STATE MOLECULE?

W. LEO MEERTS, W.A. MAJEWSKI, W. UBACHS, B.J. VAN DER MEER AND K.E. DRABE

The $S_1(^1B_1) \leftarrow S_0(^1A_1)$ transition in pyrimidine has been investigated. High resolution laser induced fluorescence spectra were obtained by crossing a well collimated molecular beam with UV radiation of an intra-cavity frequency doubled ring laser. The extreme resolution enabled us to observe the molecular eigenstates of the excited electronic state.

Most of the spectral features arising from the S_1 state could be interpreted in terms of a slightly perturbed axis switched asymmetric rotor spectrum. Perturbations are found both in the energy levels of the S_1 state and in the relative intensities of the transitions. This is in agreement with the much smaller background triplet level density in pyrimidine as compared to pyrazine[1].

Single level lifetime measurements have been carried out for rotational states up to $J' = 4$. The results suggest a lengthening of the lifetimes of the excited state with increasing values of K'.

The question put in the title will be discussed.

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[1] B.J. van der Meer, H. Th. Jonkman, J. Kommandeur, W.L. Meerts and W.A. Majewski
Chem. Phys. Lett. 92 (1982) 565

Address of Meerts and Ubachs: Fysisch Laboratorium, Katholieke Universiteit, Toernooiveld 6525 ED Nijmegen, The Netherlands
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FD3.   (9:04)

SINGLET-TRIPLET PERTURBATIONS IN PYRIMIDINE.

MAGNETIC FIELD EFFECTS ON COLLISION-INDUCED

INTERSYSTEM CROSSING *

Y. MATSUMOTO AND D. W. PRATT

Pyrimidine (1,3-diazabenzene) has been expanded in a seeded supersonic jet of helium and its laser-induced fluorescence spectrum has been recorded using a pulsed dye laser. Under these conditions, the K structure of the parallel-type 0_0^0 band is partially resolved. Exciting specific (J,K) states, we have measured the fluorescence lifetime as a function of an external magnetic field (0-250 G) and the distance from the nozzle (x/D = 25-50). Typically, the lifetime is increased by the field, owing to an increase in the triplet character of the prepared state. However, plots of τ vs. H reveal a resonant structure which suggests the presence of isolated level anticrossings between nearly pure singlet and triplet rovibronic levels. A similar structure appears in plots of the collision cross section, deduced from the x/D dependence of the lifetime, vs. the magnetic field. This similarity shows that, as suggested by theory, the cross section for collision-induced intersystem crossing increases linearly with the average triplet character of the prepared state.

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FD4.   (9:21)

DIRECT EXCITATION OF TRIPLET STATES IN A SUPERSONIC JET.

THE ROTATIONALLY RESOLVED LASER-INDUCED PHOSPHORESCENCE

SPECTRUM OF GLYOXAL *

L. H. SPANGLER, Y. MATSUMOTO, AND D. W. PRATT

The combined techniques of supersonic jet expansion, high power laser excitation, and phosphorescence detection have made it possible to obtain a rotationally resolved spectrum of the 0_0^0 band of ^3A_u glyoxal. Selection rules and intensity factors for this spin-forbidden transition will be discussed. The advantages of the direct excitation technique for studies of the structural and dynamic properties of triplet states, both in glyoxal and in other molecules, will also be discussed.

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FD5.   (9:38)

SIMULTANEOUS FLUORESCENCE EXCITATION AND DIRECT ABSORPTION OF JET-COOLED AZULENE

T. M. WOUDENBERG, M. M. CARRABBA AND J. E. KENNY

The $\Delta\bar{\nu}(cm^{-1})$ = (0,662,668,919,1299) Vibronic bands of the S_2 electronic state of Azulene seeded in a pulsed He jet, were studied using simultaneous measurement of laser absorption and laser induced fluorescence. Some discussion of Φ_f measurements and non-radiative decay rates will be presented.

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FD6.   (9:55)

THE LOWEST $n\pi^*$ TRANSITION OF PYRIMIDINE IN A FREE JET EXPANSION

W.R. MOOMAW, MM. CARRABBA, AND J.E. KENNY

The laser induced fluorescence excitation spectrum of the lowest $n\pi^*$ transition of pyrimidine has been measured in a free jet expansion. A complex system of vibronic bands is observed over a range of 3100cm^{-1}. The previously noted irregular vibrational spacings of most of the major features are reproduced in this study, and some additional closely spaced bands are clearly resolved. The broad background underlying the entire room temperature vapor absorption spectrum is absent in the free jet. The origin and other low energy bands are laser limited in their width, but some of the higher ones are clearly broadened. We also note a dramatic decrease in fluorescence quantum yield which begins just above the origin just as it does at room temperature. We will discuss several alternative approaches we are attempting to use to analyze this complex vibronic spectrum.

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FD7.   (10:12)

THE EFFECT OF HYDROGEN BONDING ON THE LOWEST $n\pi^*$
TRANSITION OF PYRIMIDINE IN A SUPERSONIC JET

M.M. CARRABBA, J.E. KENNY, AND W.R. MOOMAW

We have attempted to measure the laser induced fluorescence excitation
spectrum of several hydrogen bonded complexes of pyrimidine in a supersonic jet.
No evidence of complex formation with water was obtained. Seeding the driver
gas with hexafluoroisopropyl alcohol caused the sharp vibronic bands of
pyrimidine to disappear. Intermediate concentrations of alcohol caused the
appearance of a broad, structureless feature beginning about $4000 cm^{-1}$ above the
origin of pyrimidine at $31070 cm^{-1}$, which continued to rise to the limit of our
measurements at 275 nm. Addition of excess alcohol suppresses this feature
leading us to conclude that it is the spectrum of singly hydrogen bonded
pyrimidine. A Comparison of these data with solution spectra will be present-
ed.

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FD8.   (10:35)

GLYOXAL TRIPLET'S SPECTROSCOPY BY ANTICROSSINGS IN STRONG MAGNETIE FIELD

P. DUPRE, R. JOST, L. LEVIANDIER, M. LOMBARDI, E. PEBAY-PEYROULA

We excite single rovibronic S_1 levels of the Glyoxal molecule (CHO CHO) with
an Ar^+ pumped CW ring dye laser. The Glyoxal is cooled in a supersonic jet. We monitor
unresolved fluorescence as a function of magnetic field up to 8 T (homogeneity $\delta B/B$
$\sim 10^{-5}$ in 1 cm^3). Anticrossing accurs when rotational levels of high vibrational states
of T_1 are tuned by the field (Zeeman effect) across the singlet level excited by the
laser.

Selection rules for anticrossings are nearly identical to those for optical elec-
tric dipole transition ($\Delta N = 0, \pm 1, \ldots$)[1].

The positions in magnetic field of the anticrossings enable us to deduce the tri-
plet rotational structure and then to determine rotational constants[2].

The resolution Doppler free spectroscopy is limited in principle only by the
widths of the anticrossings. These are related to the singlet-triplet coupling V_{st} which
varies between the natural linewidth and $\sim$ 300 MHz. In fact these anticrossings have fine
and hyperfine structure. When the various peaks due to these structures overlap ($V_{st} > 25$
MHz) we use a microwave-optical double resonance method to resolve them. We are thus
able in all cases to measure the fine and hyperfine structures of the triplet levels.
We have noticed that the hyperfine structure is nearly constant for several hundreds of
observed levels (83 $\pm$ 3 MHz). This contrasts with the fine structure which varies in an
erratic manner. Experimental uncertainties are due entirely to the inhomogeneity of the
field which we measure with an NMR probe.

We have thus determined the rotational constants of several highly excited
triplet vibrational levels located around 2 800 cm^{-1} and 3 500 cm^{-1} above the fundamental
vibrational level of the electronic state T_1.

[1] T.A. MILLER and R.S. FREUND, Magnetic Induced by Electrons in Advances in
Magnetic Resonance. Editor J. WILEY and SONS.
P. DUPRE, R. JOST, M. LOMBARDI, C. MICHEL and A. TRAMER, Chem. Phys. 82 (1983) 25

[2] P. DUPRE, R. JOST, M. LOMBARDI, to be submitted to Chem. Phys.

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F09.   (10:47)

LASER SPECTROSCOPY OF THE TETRACENE-ARGON VAN DER WAALS COMPLEXES

W.M. VAN HERPEN, W. LEO MEERTS, W.A. MAJEWSKI AND A. DYMANUS

Van der Waals complexes of tetracene (T) with argon were formed in a supersonic expansion through a nozzle (150 μm). The strongly collimated molecular beam was crossed with a single frequency dye laser operating in the region 430 to 450 nm. Spectra were obtained by the technique of laser induced fluorescence. The Doppler linewidths were reduced to 15 MHz (FWHM) yielding rotationally resolved spectra for tetracene and T-Ar_n for n = 1 and 2. The structure of the latter two complexes has been deduced.

T-Ar_n complexes for n is up to 6 were observed with increasing linewidths. For n $\geq$ 3 the linewidth was too large to observe any rotational structure.

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F010.   (11:04)

THE ELECTRONIC SPECTRA OF HYDROGEN BONDED CLUSTERS OF TETRAZINE

CHERYL MORTER, CHRISTOPHER A. HAYNAM, LINDA YOUNG, AND DONALD H. LEVY

Hydrogen bonded complexes of s-tetrazine with H_2O and s-tetrazine with HCl have been formed in a supersonic free jet expansion. The laser induced fluorescence excitation spectrum of an s-tetrazine/H_2O expansion shows three features near the origin region of s-tetrazine which have been assigned to s-tetrazine$(H_2O)_n$ where n = 1, 2, or 3. In an expansion containing s-tetrazine and HCl, three peaks are also observed in the spectrum; however, these have been identified as s-tetrazine$(HCl)_1$, s-tetrazine$(HCl)_2$, and a van der Waals vibration of s-tetrazine$(HCl)_1$.

Each of these features has been rotationally resolved. The geometries for the clusters have been determined with a rotational contour generating program combined with a nonlinear least squares program. Analysis of the high resolution spectra of s-tetrazine$(HCl)_1$ and s-tetrazine$(H_2O)_1$ reveals that the hydrogen of the solvent molecule forms a hydrogen bond with the nitrogen lone pair of s-tetrazine and the resulting dimer is planar. In clusters involving more than one solvent molecule the solvent molecules bond to each other rather than the s-tetrazine ring. The rotational structure of the s-tetrazine$(HCl)_1$ van der Waals vibration band shows that this is an out-of-plane bending motion with the HCl having an average displacement of 32° from the plane of the ring.

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Address of Morter and Levy: James Franck Institute and Department of Chemistry, University of Chicago, Chicago, Illinois 60637.

FD11.   (11:21)

THE ELECTRONIC SPECTRUM OF PHENYL-TETRAZINE, Ar-PHENYL-TETRAZINE, AND THE PHENYL-TETRAZINE
DIMER

YOUNG PARK AND DONALD H. LEVY

The laser induced fluorescence spectrum of phenyl-tetrazine ($C_6H_5-C_2N_4H$), its weakly bound
dimer, and its van der Waals complex with argon were observed in a supersonic free jet. The
0-0 band of the $^1B_1-^1A_1$ ($-*\leftarrow n$) electronic transition of phenyl-tetrazine occurs at 17617.8 cm^{-1}.
Analysis of the rotational structure of phenyl-tetrazine indicated that the molecule was planar
in both its ground and excited electronic states.

Several van der Waals complexes of argon with phenyl-tetrazine were observed. Rotational
analysis showed that the simplest argon van der Waals molecule, Ar-phenyl-tetrazine, has the
argon atom out of plane above the center of the tetrazine ring at a distance of 3.34 Å.

Two tellites of the 0-0 band at -99 cm^{-1} and +36 cm^{-1} were assigned to the dimer of
phenyl-tetrazine. The two bands are produced by two different geometric isomers of the dimer.

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FD12.   (11:38)

IDENTIFICATION OF TORSIONAL TRANSITIONS IN THE SUPERSONIC JET SPECTRUM OF
MONO-METHYL TETRAZINE

C.J. Seliskar and M.A. Leugers

Identification of the strong torsional transitions, with m'=m''=±1 and delta m equal to zero, in
the high-resolution laser excitation molecular beam spectrum of the methyl tetrazine 5613 Å origin
band recently published by Haynam and Levy (1) has been made. Use of their published tetrazine
frame rotational constants with $A_T = 5.3403$ cm^{-1}, $\Delta A_T = -0.034$ cm^{-1} results in predicting the
positions of the torsional transitions for J up to 3 to within about .001 cm^{-1} precision. However,
line positions for larger values of J are not adequately calculated using these constants in the
asymmetric top/free internal rotor model (2), the fit worstening with increasing J. Reasons for
this discrepancy are discussed.

Assumption of an equilibrium distribution over both rotation and torsion states for a specified
temperature does not quantitatively reproduce the observed molecular beam spectrum intensities.
However, a simple model based on a suggestion of Smalley, et al. (3) does produce the observed
spectral intensities in at least the simplest of the Haynam and Levy (1) spectra. Indeed, this simple
model, with $T_{rot} = 0.50K$ and $T_{m=1} = 5.0K$ reproduces the published 500 PSI backing-pressure
spectrum on a line-for-line basis.

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FD13. (11:55)

TWO-PHOTON FLUORESCENCE EXCITATION SPECTRUM OF BENZOTRIFLUORIDE

S. DORAISWAMY AND N. PERIASAMY

The $\widetilde{A}\ ^1B_2 - \widetilde{X}\ ^1A_1$ two-photon fluorescence excitation spectrum of benzotrifluoride in the gas phase has been recorded and analysed in the total energy range of 37800 cm^{-1} to 40300 cm^{-1} using both linearly and circularly polarized light from a Nd-YAG pumped dye laser. The band system comprised of two groups, one group being unaffected and the other diminishing in intensity under circular polarization of the laser beam. The two-photon tensor patterns can be used to understand these behaviour. The intensity ordering of the bands in the two-photon spectrum is $14^1_0 \gg 1^1_0 > 0^0_0$ (Wilson numbering convention) while in one-photon spectrum the origin band is the strongest. The spectral features of benzotrifluoride are compared with fluorobenzene and toluene.

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FD14. (12:12)

STIMULATED EMISSION PUMPING OF ACETYLENE: EVIDENCE FOR QUANTUM CHAOTIC BEHAVIOR NEAR 28000 CM^{-1} OF EXCITATION?

R. SUNDBERG, E. ABRAMSON, D. IMRE, G. SCHERER, R.W. FIELD, AND J.L. KINSEY

Last year at this conference, we described the use of Stimulated Emission Spectroscopy to probe the structure of the $X^1\Sigma^+_g$ state of C_2H_2 at 28,000 cm^{-1} of vibrational energy above the ground state. These highly vibrationally excited levels are accessed by stimulated emission from the $v_3=2$ and 3, K=1 levels of the trans-bent $\widetilde{A}^1A_u$ excited state. In contrast to overtone spectroscopy, which populates primarily C-H overtones of u-symmetry, SEP accesses g-symmetry levels with C-C and trans-bending excitation.

The spectrum is characterized by clumps of narrowly spaced lines (~10 lines per cm^{-1} in a 2 cm^{-1} wide clump). All of the lines in a given clump arise from transitions into levels with the same lower-state J-value. Thus, the fine structure in each clump is of a purely vibrational nature.

The unique qualities of these spectra make it possible to apply to a real molecule some of the suggested criteria for quantum chaos. Analysis of the level spacing and intensity distributions indicates that the molecular dynamics of highly excited C_2H_2 samples a large fraction of its energetically accessible phase space, a characteristic which is consistent with chaotic molecular dynamics.

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FD15.

STIMULATED EMISSION SPECTROSCOPY OF ACETYLENE: THE $\tilde{X}^1\Sigma_g^+$ STATE AT 10,000-14,000 CM^{-1}

G. SCHERER, Y. CHEN, S. HALLE, J.L. KINSEY, AND R.W. FIELD

Stimulated Emission Pumping (SEP) is a variant of Optical-Optical Double Resonance, utilizing two pulsed dye lasers. The first laser, the PUMP, is tuned to populate a single rotation-vibration level of the $\tilde{A}^1A_u$ state of $^{12}C_2H_2$. The second laser, the DUMP, stimulates emission downward from the prepared level into a vibrationally excited level of the electronic ground state, $\tilde{X}^1\Sigma_g^+$. The SEP signal is seen as a decrease in $\tilde{A}{\rightarrow}\tilde{X}$ side fluorescence when the DUMP laser is on resonance. Because the $\tilde{A}$-state of acetylene is trans-bent in its equilibrium configuration, Franck-Condon factors permit us to DUMP into vibrational levels with primarily trans-bending character.

In the present talk, we will discuss the SEP spectrum of the $\tilde{X}^1\Sigma_g^+$ state of acetylene at ~10,000-14,000 cm^{-1} of energy above the vibrational ground state. Experimental details of the SEP technique will also be given.

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FD16.

DIPOLE MOMENTS IN THE OUT-OF-PLANE BENDING LEVELS OF $\tilde{A}^1A_2$ FORMALDEHYDE-h_2 AND -d_2

A. ZABLUDOFF, P.H. VACCARO, M. CARRERA, J.L. KINSEY, AND R.W. FIELD

Stark-Induced Quantum Beat Spectroscopy is used to measure dipole moments in the ν_4 vibrational levels of the first excited singlet state in formaldehyde-h_2 and -d_2. The polarization of the incident laser pulse is perpendicular to the direction of a 0 to 5 kV/cm static electric field. Evolution of the coherent superposition produced between Stark-split M-sublevels of a selected $\tilde{A}^1A_2$ rotation-vibration level exhibits a quantum interference effect which is observable in the undispersed fluorescence. Analysis of these oscillations yields dipole moments with a precision in excess of 1 part per 1000. The results can be interpreted in terms of S_1~S_0 perturbations and vibronic coupling models.

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FD17.

ROTATIONAL RELAXATION IN THE $v_4=1$ VIBRATIONAL LEVEL OF H_2CO $\tilde{A}^1A_2$ BY TRANSIENT GAIN SPECTROSCOPY

P.H. VACCARO, R.L. REDINGTON, J. SCHMIDT, J.L. KINSEY, AND R.W. FIELD

Rotational relaxation in the $v_4=1$ out-of-plane bending mode of $\tilde{A}^1A_2$ formaldehyde is investigated by means of a novel, folded double-resonance technique. A pulsed dye laser is tuned to coincide with a specific rovibronic transition in the $\tilde{A}^1A_2\leftarrow\tilde{X}^1A_1$ 4_0^1 band. The transient gain appearing on a copropagating cw probe laser, coincident with the $2_1^0 3_1^0 4_1^1$ $13_{2,12}\rightarrow13_{1,13}$ transition, samples total depopulation rates as well as rotational state-to-state cross sections. Results verify that relaxation in the formaldehyde $\tilde{A}^1A_2$ $v_4=1$ level occurs with a rate approximately ten times the gas kinetic collision rate. The sensitivity of transient gain spectroscopy, in conjunction with its superior spectral $(0.05\ cm^{-1})$ and temporal (6 nsec) resolution, is shown to be especially useful in the H_2CO $\tilde{A}^1A_2$ system where the radiative rate is slow compared to the strongly rotation level dependent rates of nonradiative processes.

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